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Treatment and Recovery of Fluoride and Nitrate Industrial Wastes. Phase II

Grumman Aerospace Corp, Bethpage, N Y

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Laboratory and pilot-scale techniques to treat selected metal-finishing solutions and rinse waters containing fluorides and nitrates were developed and successfully demonstrated. Lime-treatment parameters were optimized for various fluoride and nitrate influent levels. Ion-exchange techniques reduced the fluoride and nitrate concentrations of rinse waters to three and ten parts per million, respectively. Pilot-scale centrifugal techniques to separate precipitated calcium fluoride and metal hydroxide sludges were developed. The nitrate concentration of centrifuged effluents was reduced from 28,000 to less than five parts per million by passing the effluents through a thin-film, mechanically aided evaporator. Fluoride concentration was reduced from 117,000 to less than one part per million. The potential feasibility of using calcium fluoride sludge as a strength-maintaining additive for concrete was shown. Greenhouse tests indicated that concentrated calcium nitrate recovered from mechanically aided evaporation is a beneficial and practical plant fertilizer. Economic and production scale-up plans for process solution and rinse water treatment are also presented.

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March 1978

TREATMENT AND RECOVERY OF FLUORIDE AND NITRATE INDUSTRIAL WASTES

PHASE II

by

Christian J. Staebler, Jr.
Grumman Aerospace Corporation
Bethpage, New York 11714

Project No. S800680

Project Officer

Hugh B. Durham
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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FOREWORD

When energy and material resources are extracted, processed, converted and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes the laboratory and pilot-scale techniques that were developed to treat selected chemical processing solutions and rinse waters containing fluorides and nitrates, and to recover usable byproducts. The results of this study can be used to design a production-scale, waste treatment system for fluoride- and nitrogen-containing solutions. This report should be of value to industrial users of metal processing solutions such as aerospace, automotive, building construction, consumer product and marine equipment firms. The Industrial Pollution Control Division should be contacted for further information on this subject.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Laboratory and pilot-scale techniques to treat selected aerospace- and metal-working-industry chemical processing solutions and rinse waters containing fluorides and nitrates were developed and successfully demonstrated. Lime-treatment parameters such as temperature, retention time, pH, and slurry concentration were optimized for various fluoride and nitrate influent levels in chemical processing solutions to minimize the fluoride and nitrate effluent levels. Ion-exchange techniques were developed that reduce the fluoride and nitrate concentrations of rinse waters to levels of 3 and 10 ppm, respectively.

Pilot-scale centrifugal techniques to separate precipitated calcium fluoride and metal hydroxide sludges were developed. The nitrate concentration of centrifuged effluents was reduced from 28,000 to less than 5 ppm in the optimized pilot-scale system by passing these effluents through a thin-film, mechanically aided evaporator. The fluoride concentration was reduced from 117,000 to less than 1 ppm in the pilot treatment system.

Chemical and mechanical property tests showed the potential feasibility of using calcium fluoride sludge as a strength-maintaining additive for concrete. Concentrated calcium nitrate recovered from the mechanically aided evaporator was evaluated in conjunction with the Cornell University Extension Research Farm on Long Island as a potential growth-enhancement material. Greenhouse tests indicated that this material is a beneficial and practical plant fertilizer.

The economics and production scale-up plans for ion-exchange rinse water treatment and process solution treatment are also presented.

The report was submitted in fulfillment of Project S800680 by Grumman Aerospace Corporation under the (partial) sponsorship of the Office of Research and Development, U.S. Environmental Protection Agency. This report covers a period from August 31, 1973 to March 31, 1976, and work was completed as of June 30, 1976.

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SECTION 1

INTRODUCTION

A steadily increasing number of applications for titanium, super-alloys, refractory metals and aluminum in military and commercial projects is making it necessary to expand the use of fluoride- and nitrate-containing solutions for cleaning, deoxidizing, descaling and other chemical operations. Mounting public concern about environmental pollution and more stringent government regulations have put increased pressure on metalworking industries to use non-polluting fluoride and nitrate waste disposal procedures.

The increasing volumes of fluoride- and nitrate-containing processing solutions and rinse waters being generated, however, are making existing methods of disposing of these solutions prohibitively expensive. Most aerospace firms use vendors to dispose of waste solutions. Because vendors may sometimes use questionable treatment and disposal methods, the firms which supplied the waste solutions can be held responsible for vendor-caused pollution damage. Also, because vendors may not normally regenerate fluoride and nitrate wastes, the pollution problems may merely be transferred from one location to another. This project was initiated, therefore, to develop a comprehensive fluoride and nitrate waste treatment technology for chemical processing solutions and rinse waters used in the aerospace and metalworking industries. The fluoride and nitrate treatment approach was based on the use of lime precipitation and mechanically aided evaporation for process solutions and ion-exchange for rinse waters.

SECTION 2

CONCLUSIONS

- Pilot testing of the two-stage ion-exchange treatment system under repeated exhaustion and regeneration conditions showed that Rohm and Haas Amberlite IRA-400 resin in conjunction with Alcoa F-1 activated alumina is an effective ion-exchange system for removal of fluorides and nitrates from process solution rinse waters and conditioning of rinse waters for recycle.

- Process solution rinse waters having average influent fluoride and nitrate levels of 12 ppm and 60 ppm, respectively, can be reduced to fluoride and nitrate levels of less than 3 ppm and 10 ppm, respectively, using ion-exchange treatment.

- Physical and chemical property tests performed on the Amberlite IRA-400 resin after 10 cycles of exhaustion and regeneration showed that there was no decrease in resin capacity compared to starting material.

- Any silica fouling of the Amberlite IRA-400 resin can be reduced or eliminated by using hot caustic 40°C (120°F) to regenerate the resin.

- The ion-exchange regeneration waste from the Amberlite IRA-400 resin and the F-1 activated alumina can be treated by addition of dry lime, followed by solids separation for fluoride removal and mechanically aided evaporation for nitrate removal and concentration.

- Typical aerospace and metalworking industry chemical processing solutions such as nitric-hydrofluoric acid descaling, aluminum deoxidizer, and alodine aluminum conversion coating can be treated to final effluent fluoride and nitrate concentrations of less than 1 and 5 ppm, respectively.

- Chemical granular quicklime (CaO) is the most effective low-cost material for fluoride and dissolved-metal treatment of acid-containing chemical process solutions.

- Chemical and mechanical property tests showed the potential feasibility of using calcium fluoride sludge as a strength-maintaining additive for concrete.

- The nitrate concentration of lime-treated and separated effluents of spent chemical process solutions was reduced from 28,000 to less than 5 ppm by passing these effluents through a thin-film mechanically aided evaporator.

- Calcium nitrate recovered from the thin-film mechanically aided evaporator proved to be an effective plant fertilizer. Greenhouse tests conducted in

conjunction with Cornell University's Extension Research Farm showed the potential growth-enhancement that could be achieved.

- A steam economy of 80% was achieved in the thin-film mechanically aided evaporator for concentration of the nitrate containing influent to 50% solids at feed rates up to 155 kg/hr·m^2 (32 lb/hr·ft^2).

- The cost breakeven point for waste treatment materials (lime and steam) versus sale of recovered calcium nitrate at the current selling price, $330/metric ton ($300/ton), occurs at 6000 ppm nitrate in the evaporator feed. Nitrate evaporator feeds containing 38,000 ppm of nitrate would show a cost advantage of $0.05/l ($0.19/gal).

- Data generated in the studies to remove fluorides and nitrates from process solutions and rinse waters made it possible to prepare production scale-up plans.

SECTION 3

RECOMMENDATIONS

This technology development program established the pilot data required to prepare production scale-up plans for a waste treatment system capable of removing fluorides and nitrates from chemical process solutions and rinse waters used by the aerospace and metalworking industries. This program also made it abundantly clear that a production-scale demonstration program should be carried out next to verify the economic and treatment quality aspects of the pilot waste treatment process.

If the following development efforts were performed, aerospace and metalworking firms would be able to implement the fluoride and nitrate waste treatment process in their production plants with a high degree of confidence:

- Operating parameters have been developed for pilot operation of the waste treatment system and scale-up of these parameters has been predicted; verification of these operating parameters should be made on a production facility in order to show that scale-up has resulted in the optimum operation with respect to effluent quality and economics for each of the process solutions being tested. Operating parameters that should be considered include feed flow rates, treatment levels, separation levels, hold times and recycle capabilities.

- Feasibility of a continuous operation treatment system using in-line mixers for process waste reaction with lime and polyelectrolyte additions should be determined. Incorporation of an automatic control system should be evaluated to ensure treatment level reliability and fail safe operation.

- Quality control test requirements necessary to maintain optimum performance for the various treatment steps must be established.

- Further evaluation of polyelectrolyte flocculant requirements to determine separation performance is recommended. The effects of these flocculants on re-use of calcium fluoride as a concrete additive or phase-change material and calcium nitrate as a fertilizer should also be determined.

- Requirements for final effluent treatment before re-use or discharge, such as pH adjustment and filtration to remove suspended solids, should be determined, and specific procedures for this treatment should be established.

- Economic analysis for the finalized treatment system design should be made including equipment, labor and utilities to provide a complete basis for industry acceptance of the proposed treatment design.

- Additional field testing of the waste calcium nitrate fertilizer should be performed to verify plant yield, nitrogen present in plant during various growth stages, residual soil nitrogen, change in soil pH and toxicity, if any.

- The calcium fluoride waste should be evaluated as a low-cost phase-change material for thermal energy storage. Development efforts would include establishing additives to form a eutectic, phase diagrams, heat of fusion, thermal conductivity, containment materials, effect of impurities and compound stability.

- The following information must be established before concrete containing calcium fluoride sludge can be used for construction:

  - Maximum amount of sludge that can be added to maintain or increase concrete strength

  - Short- and long-term aging strength through structural testing

  - Long-term leachability, slump, air content and degree of strength degradation due to environmental exposure.

- The applicability of the fluoride and nitrate waste treatment system to other aerospace and metalworking industry wastes should be established. Where necessary, treatment techniques should be developed and tested to provide complete waste treatment procedures for these solutions.

SECTION 4

ION-EXCHANGE TREATMENT OF RINSE WATERS FOR FLUORIDE AND NITRATE REMOVAL

APPROACH

This phase of the program was directed toward the removal of fluorides and nitrates from rinse waters so that they may be recycled or disposed of in a non-polluting condition. The approach taken involved two-stage ion-exchange treatment -- the first for fluoride and nitrate removal, and the second for pH adjustment and fluoride polishing.

STUDY AREAS

Pilot evaluation of the ion-exchange operating parameters for fluoride and nitrate removal involved the following:

- Set-up of the materials and equipment
- Development of column exhaustion and regeneration procedures
- Generation of breakthrough data
- Establishment of pH and heavy-metal cation control
- Evaluation of resin stability
- Determination of production scale-up and economic factors.

BACKGROUND

Two-stage, ion-exchange treatment of titanium chemical-milling rinse waters to remove fluorides and nitrates was shown to be feasible by the initial EPA/Grumman program, "Treatment and Recovery of Fluoride Industrial Wastes," Project S800680 (12070HGH). Two, 1982-cm^3 (0.07-ft^3) columns -- one containing Rohm and Haas Amberlite IRA-400 ion-exchange resin and the other Alcoa F-1 activated alumina -- were used in series for fluoride and nitrate removal, and fluoride polishing and pH adjustment, respectively. This laboratory evaluation showed that the fluoride content of titanium chemical-milling rinse waters was reduced to less than 1 ppm, thereby permitting recycling or disposal into discharge basins of the treated rinse waters. As a result, pilot testing of the two-stage, ion-exchange treatment system was recommended to determine operating parameters for production implementation. These were evaluated in terms of breakthrough capacity and the exchange capacity of the

resin for the influent system under study. Knowledge of the breakthrough capacity makes production scale-up possible.

EQUIPMENT AND MATERIALS

Two, 0.02832-m^3 (1-ft^3) acrylic columns, 15.2 cm (6 in) in diameter by 2.0 m (80 in) high, were used for the pilot tests. Valves and piping were made from polyvinyl chloride plastic. The system (Figure 1) was designed to permit operation of the columns either in series or individually to facilitate regeneration.

Rohm and Haas' Amberlite IRA-400 ion-exchange resin was selected to remove fluorides and nitrates from rinse waters based on the results of the previous program. Alcoa's F-1 activated alumina was used in series with the Amberlite IRA-400 ion-exchange resin because the previous program had shown that it did polish fluorides and adjust the pH to the process level. This made it possible to re-use the process rinse waters, even though Alcoa F-1 activated alumina did not remove a significant amount of fluorides from the rinse waters (see material properties in Table 1).

DETERMINATION OF COLUMN OPERATING PARAMETERS

Procedure

Determination of equilibrium breakthrough capacity was accomplished by subjecting the columns to repeated exhaustion and regeneration cycles. Fluoride and nitrate concentrations, pH and conductivity were monitored during each exhaustion cycle. Breakthrough capacity was determined as the point at which fluoride and nitrate concentrations in the effluent exceeded 3 and 10 ppm, respectively.

A standard rinse water solution was prepared from concentrated solutions to give the average fluoride and nitrate concentrations, 12 and 60 ppm, respectively, in the actual titanium chemical-milling rinse water. Trace amounts of heavy-metal cations were also included to simulate the production rinse water (Table 2).

Exhaustion and Regeneration

Flow rate of the test rinse water ranged from 1.9 to 5.7 l/min (0.5 to 1.5 gpm) for each of the exhaustion cycles which involved 2,300 to 3,000 l (600 to 800 gal) of influent. Samples taken during the exhaustion cycle were analyzed for fluoride and nitrate concentrations, pH and conductivity. Column regeneration was accomplished by passing 68 l (18 gal) of 4% sodium hydroxide (NaOH) solution through the Amberlite IRA-400 resin at a rate of 1.9 l/min (0.5 gpm). The column was then rinsed with 189 l (50 gal) of water at a rate of 1.9 l/min (0.5 gpm). Alcoa's F-1 activated alumina required 136 l (36 gal) of 4% sulfuric acid (H_2SO_4) passed through at a rate of 1.9 l/min (0.5 gpm) for regeneration. This was followed by a 189 1 (50 gal) water rinse at a rate of 1.9 l/min (0.5 gpm). Samples taken during regeneration were analyzed for fluoride and nitrate concentrations and pH to determine the degree of regeneration (see test conditions in Table 3).

BREAKTHROUGH CAPACITY

Breakthrough capacity to reduce fluoride: nitrate concentration from 12:60 ppm to less than 3:10 ppm was determined on ten exhaustion cycles. Seven of these cycles

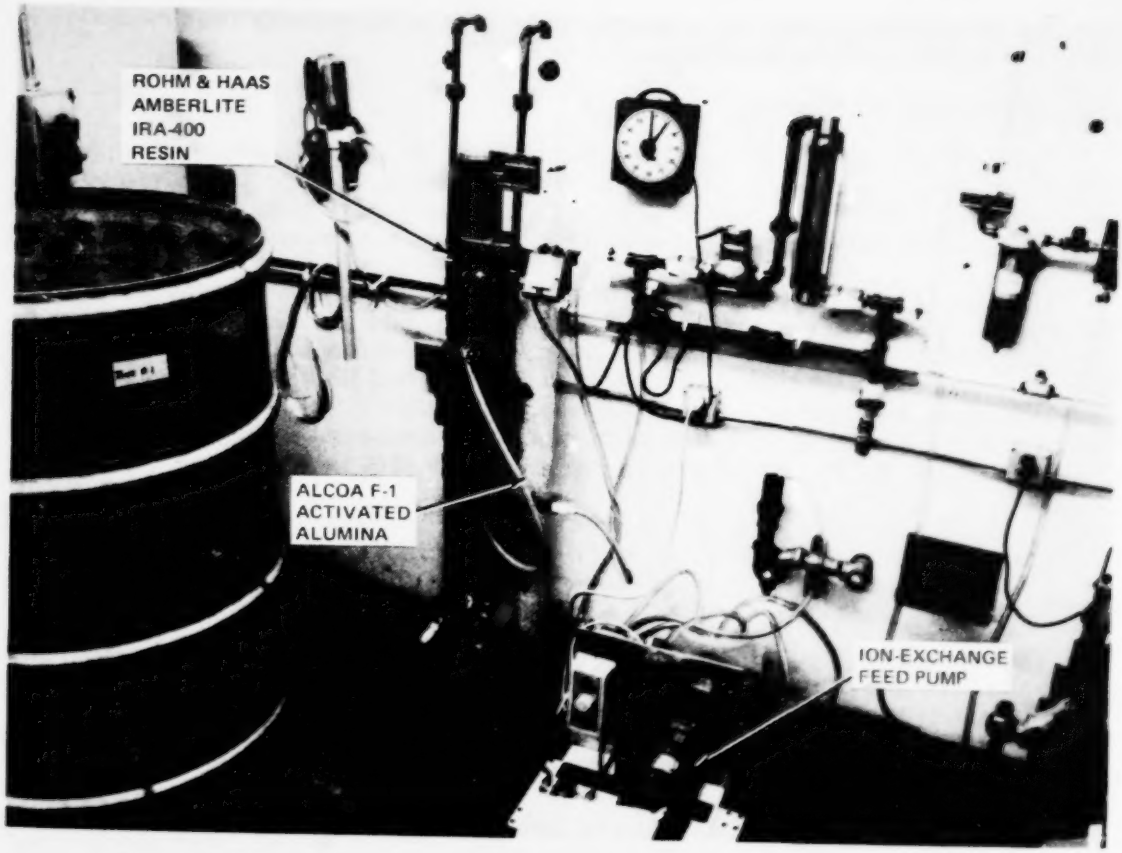


Figure 1. Two-stage ion-exchange system for rinse water treatment.

TABLE 1. PROPERTIES OF ION-EXCHANGE TREATMENT MATERIALS

Material	Property
Amberlite IRA-400 Ion-Exchange Resin	• Chemical: Strongly basic material consisting of an 8% crosslinked polystyrene matrix of the trimethylbenzyl-ammonium type • Bulk Density: 700 kg/m^3 (44 lb/ft^3) • Size : 297-841 microns (50-20 U. S. standard mesh) • Void Volume: 40-45% • Moisture Content (drained): 42-48% by weight
F-1 Activated Alumina	• Chemical: Porous form of aluminum having a high surface area • Bulk Density: 880 kg/m^3 (55 lb/ft^3) • Size: 2.38-6.35 mm (8 U. S. standard mesh to 1/4 inch) • Moisture Content (drained): 44% by weight

TABLE 2. TITANIUM CHEMICAL MILLING RINSE WATER ANALYSIS

Ion	Concentration, ppm Range	Avg
F^-	1 - 36	12
$NO_3^-(N)$	23 - 120	60
Al	0.5 - 6.7	1.9
Ti	1.5 - 9.9	4.2
V	< 0.4 - 0.9	0.4
Fe	0.2 - 1.8	0.5
Mn	< 0.5 - 0.5	< 0.5
Cu	0.3 - 0.9	0.5
Zn	< 0.1 - 0.2	0.1

were run at 1.9 l/min (0.5 gpm), two at 5.7 l/min (1.5 gpm) and one at 3.8 l/min (1.0 gpm). Because the resin was supplied in a super-regenerated state (400 kg $NaOH/m^3$ resin or 25 lb/ft^3), the first cycle at 1.9 l/min (0.5 gpm) and the second cycle at 3.8 l/min (1.0 gpm) showed a high breakthrough capacity - greater than 2,270 l (600 gal) (Figures 2 and 3).

Subsequent tests at 1.9 l/min (0.5 gpm) showed that the average breakthrough capacity was 1,820 l (480 gal) for fluoride and 1,630 l (430 gal) for nitrate (Table 4, Figures 4 through 9). These capacities will be used for scale-up to production levels. Test data at 5.7 l/min (1.5 gpm) showed that breakthrough capacity does not vary significantly with flow rate in this range (Table 4, Figures 10 and 11). As a result, this flow rate will be used for production scale-up to minimize resin requirements. Additional testing over a wider range of flow rates is needed, however, to more clearly define the effect of flow rate on breakthrough capacity.

Although changes in the influent concentration may slightly affect breakthrough capacity, the laboratory studies from the initial program showed that occasional concentration spikes (to 60 ppm of fluoride) can be treated to reduce fluoride concentration to the required level (less than 3 ppm) with the resin volume designed for the standard influent concentration (12 ppm of fluoride). Thus, a system designed to handle the average concentration can be expected to handle occasional concentration spikes.

Regeneration also affects the exchange capacity of the resin. At a regeneration level of 96 kg $NaOH/m^3$ (6 lb/ft^3) of Amberlite IRA-400 resin, the total anion exchange capacity is 25.2-27.5 kg $CaCO_3/m^3$ (11-12 kgr/ft^3) of resin. The breakthrough capacity under these conditions represents an exchange capacity usage of 75% of the total capacity, including the water background (silica, alkalinity and free-mineral acidity). Use of hot (49°C/120°F) caustic regeneration may increase the exchange capacity

TABLE 3. SUMMARY OF EXHAUSTION AND REGENERATION CONDITIONS

Test Condition	Amberlite IRA-400	F-1 Activated Alumina
Column Volume, cm^3 (ft^3)	28,320 (1)	28,320 (1)
Influent		
Concentration: 12 ppm F^-/60 ppm NO_3^- (N)		
pH: 2.7		
Conductivity: 120-2,000 μmho/cm		
Exhaustion		
Flow Rate: 1.9-5.7 l/min (0.5-1.5 gpm)		
Regeneration		
Regenerant Concentration	4% NaOH	4% H_2SO_4
Flow Rate, l/min (gpm)	1.9 (0.5)	1.9 (0.5)
Level, kg/m^3 (lb/ft^3) regenerant/resin	96 (6)	192 (12)
Rinse Rate, l/min (gpm)	1.9 (0.5)	1.9 (0.5)
Rinse Water Usage, l (gal)	190 (50)	190 (50)

TABLE 4. SUMMARY OF BREAKTHROUGH DATA

Ion	Ion Concentration, ppm		Flow Rate, l/min (gpm)	Breakthrough Capacity, l (gal)		No. of Tests*
	Influent	Breakthrough		Range	Avg	
Fluoride	12	3	1.9 (0.5)	1420–2080 (375–550)	1820 (480)	6
			5.7 (1.5)	1700–1800 (450–475)	1700 (450)	2
Nitrate	60	10	1.9 (0.5)	1325–1890 (350–500)	1630 (430)	6
			5.7 (1.5)	1610–1700 (425–450)	1700 (450)	2

*Does not include tests affected by super-regeneration of resin as supplied by the manufacturer.

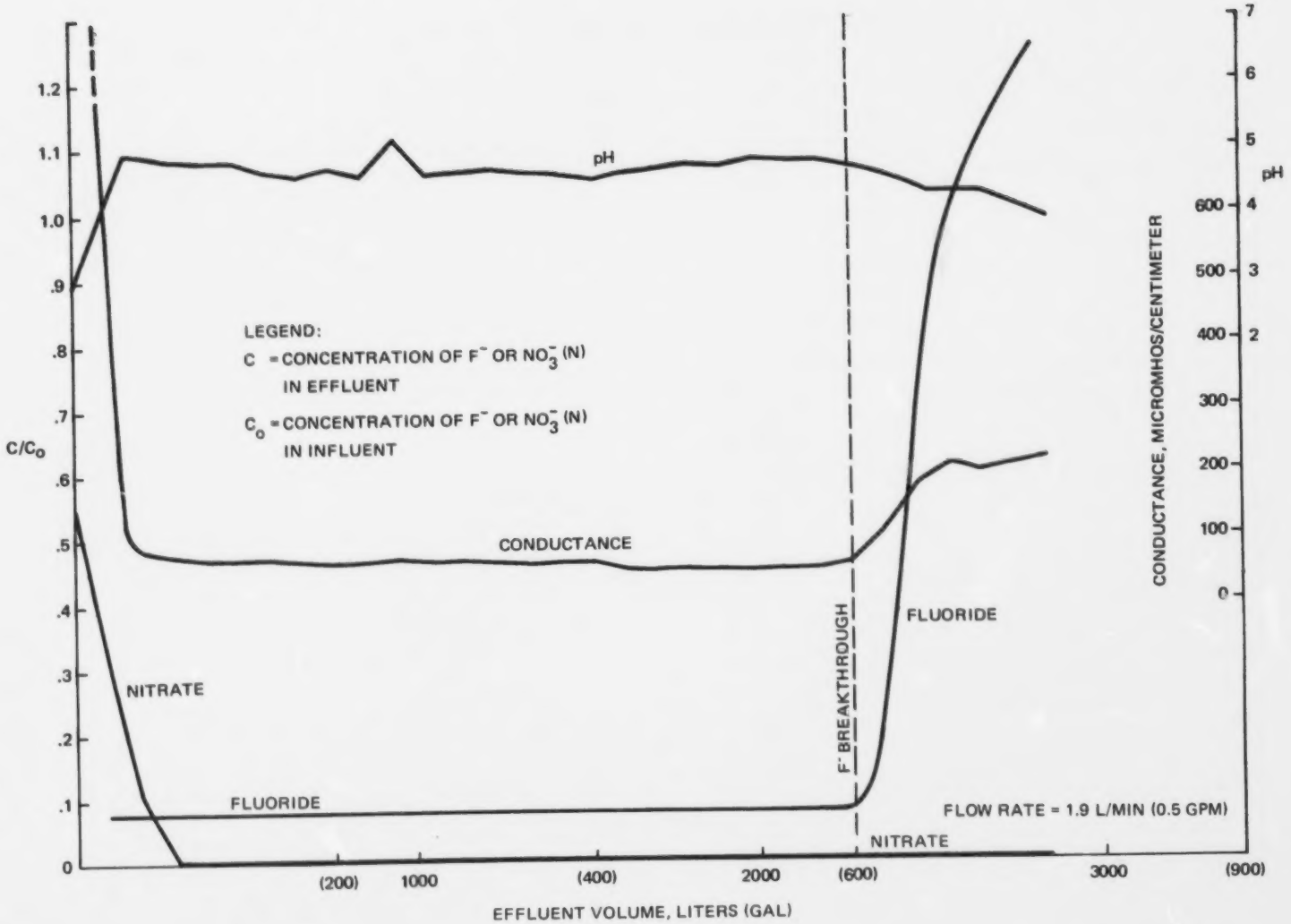
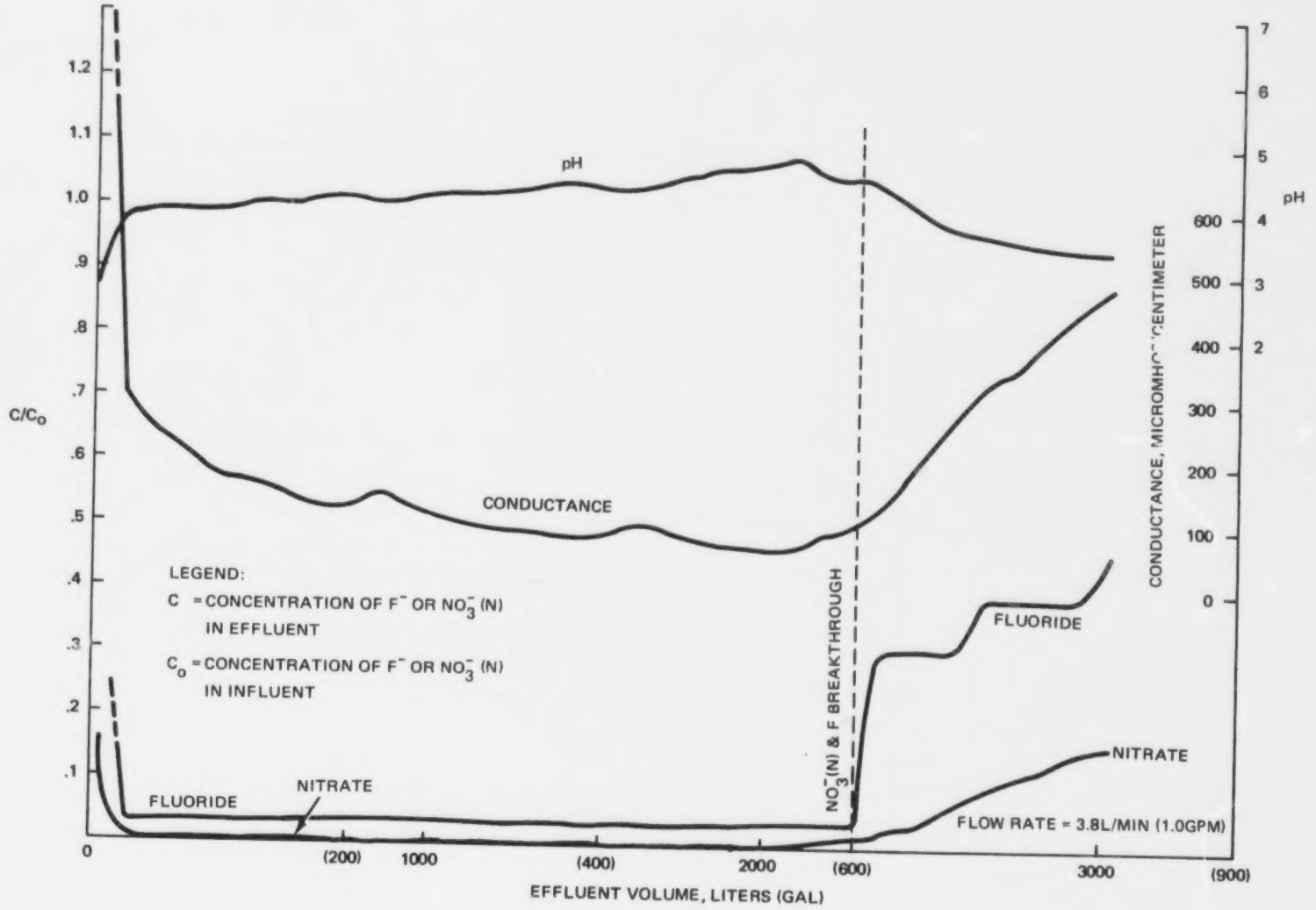


Figure 2. Ion-exchange breakthrough test no. 1.



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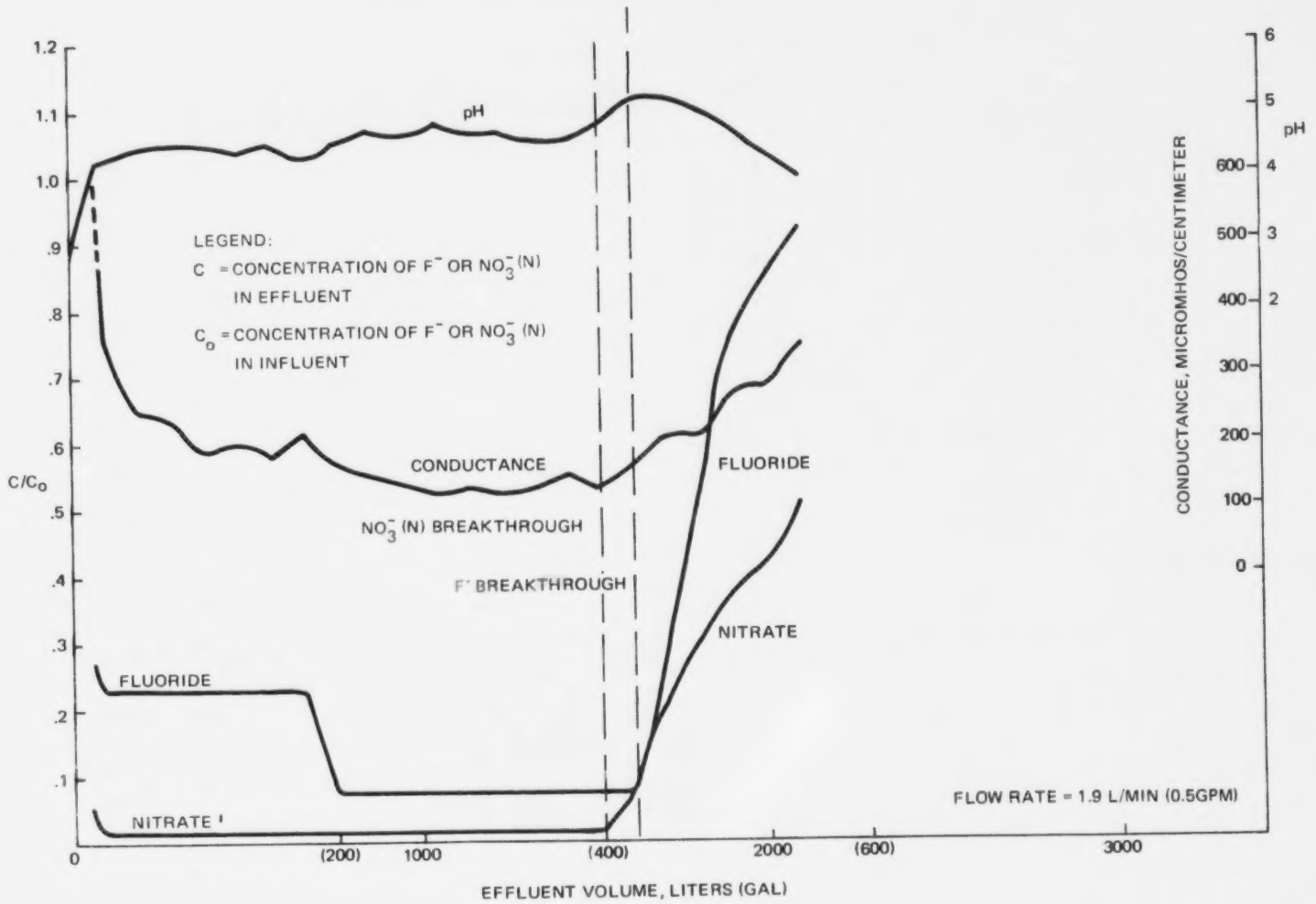

Figure 4. Ion-exchange breakthrough test no. 4.

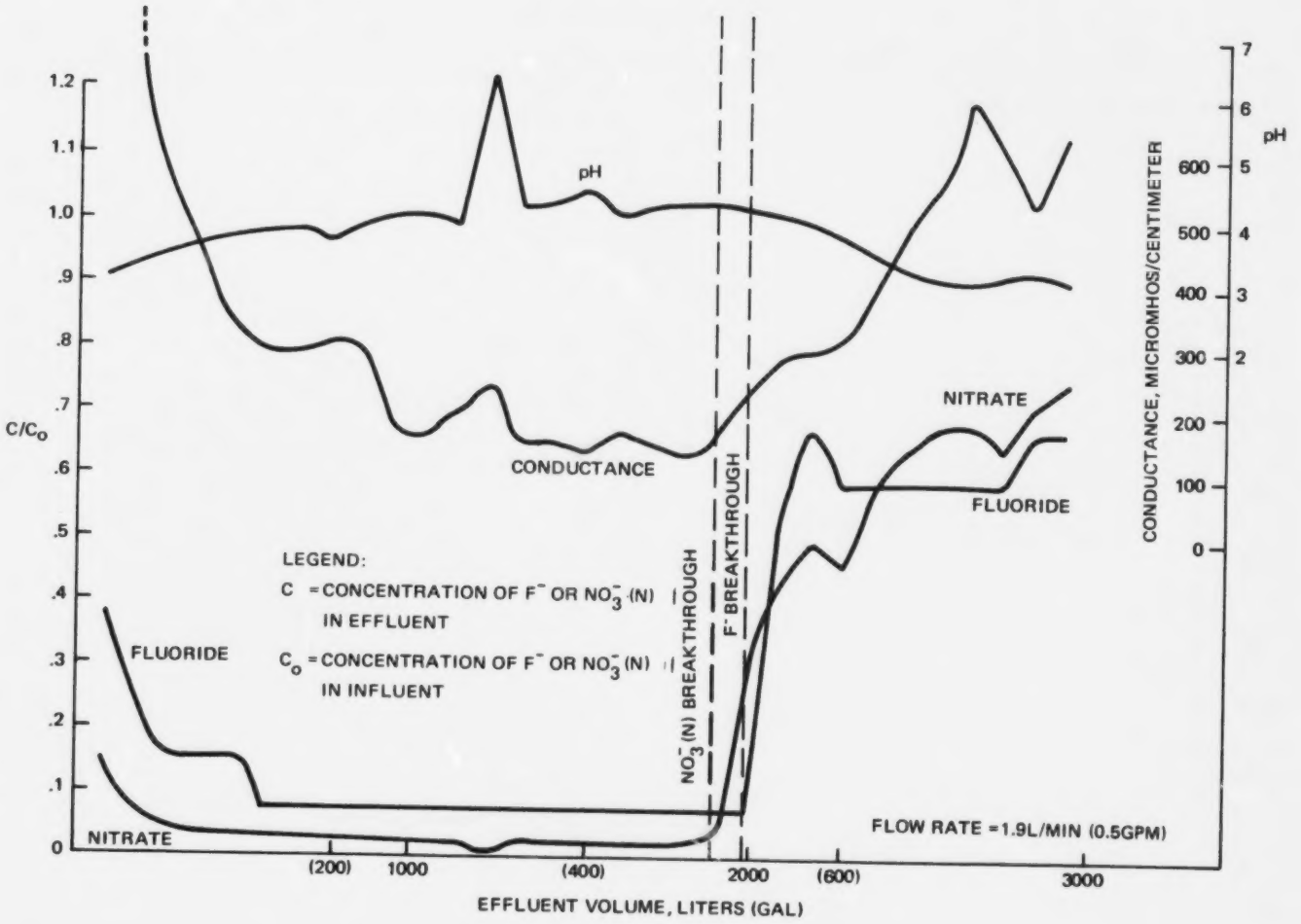

Figure 5. Ion-exchange breakthrough test no. 5.

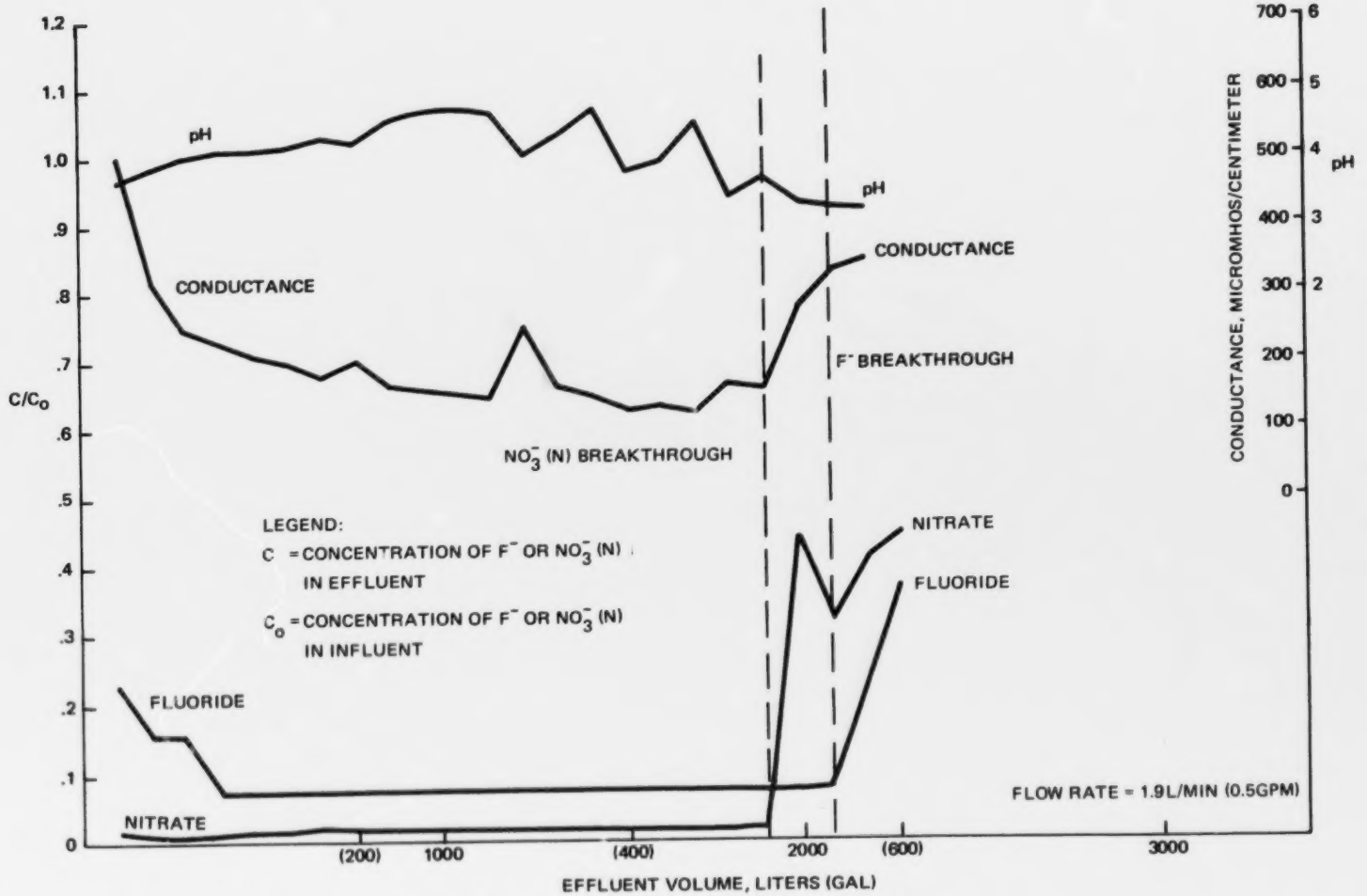

Figure 6. Ion-exchange breakthrough test no. 7.

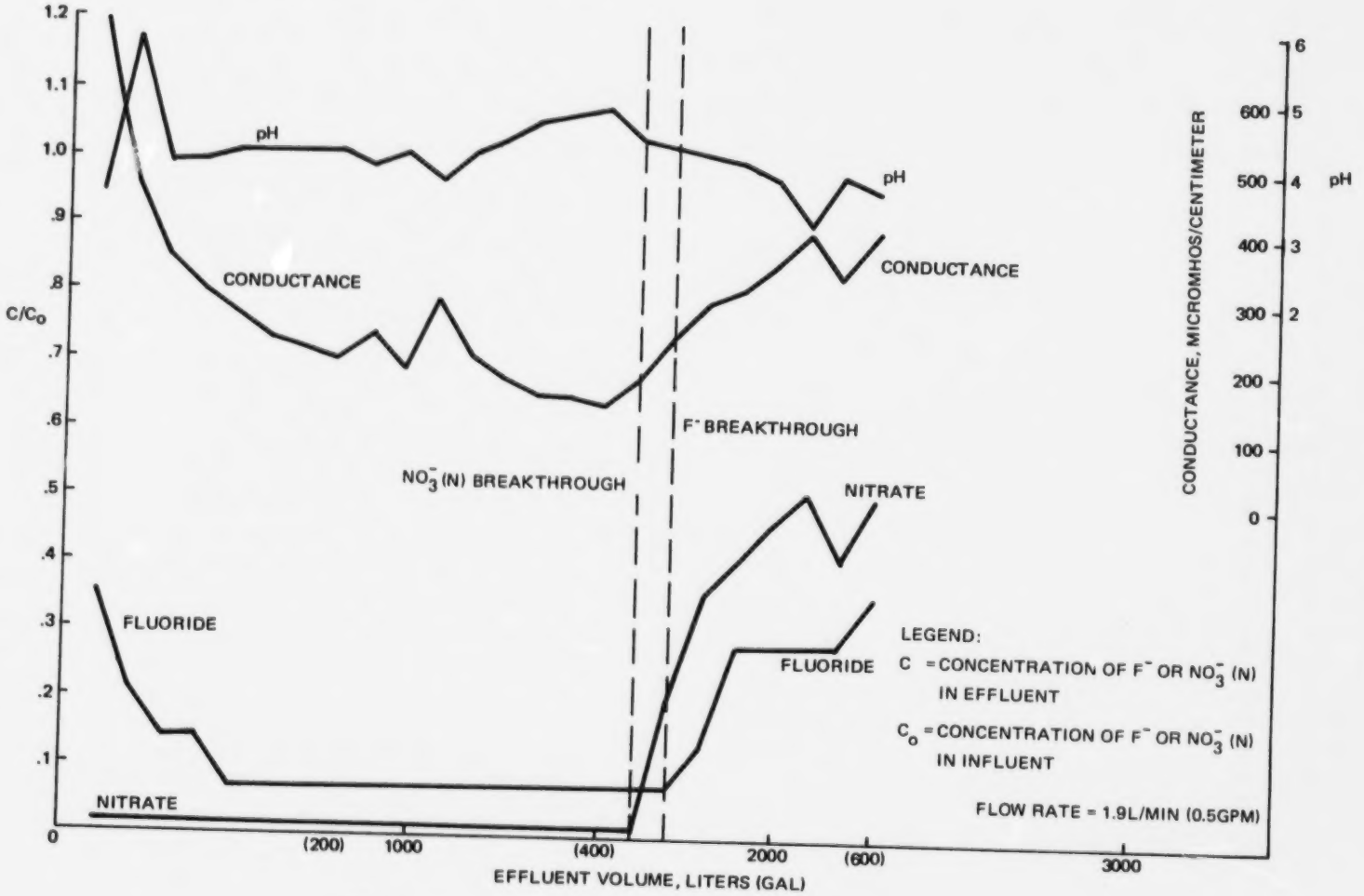

Figure 7. Ion-exchange breakthrough test no. 8.

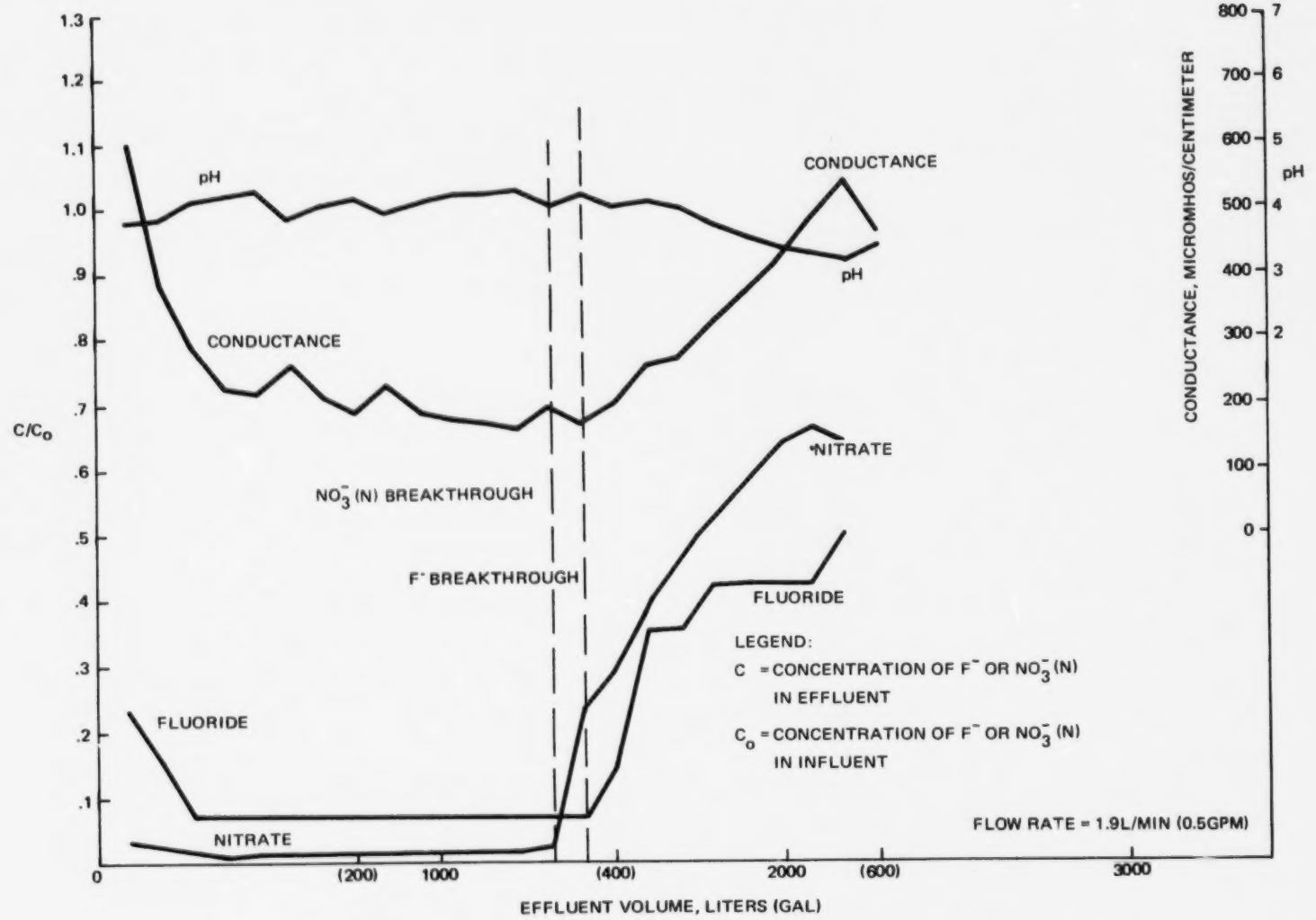

Figure 8. Ion-exchange breakthrough test no. 9.

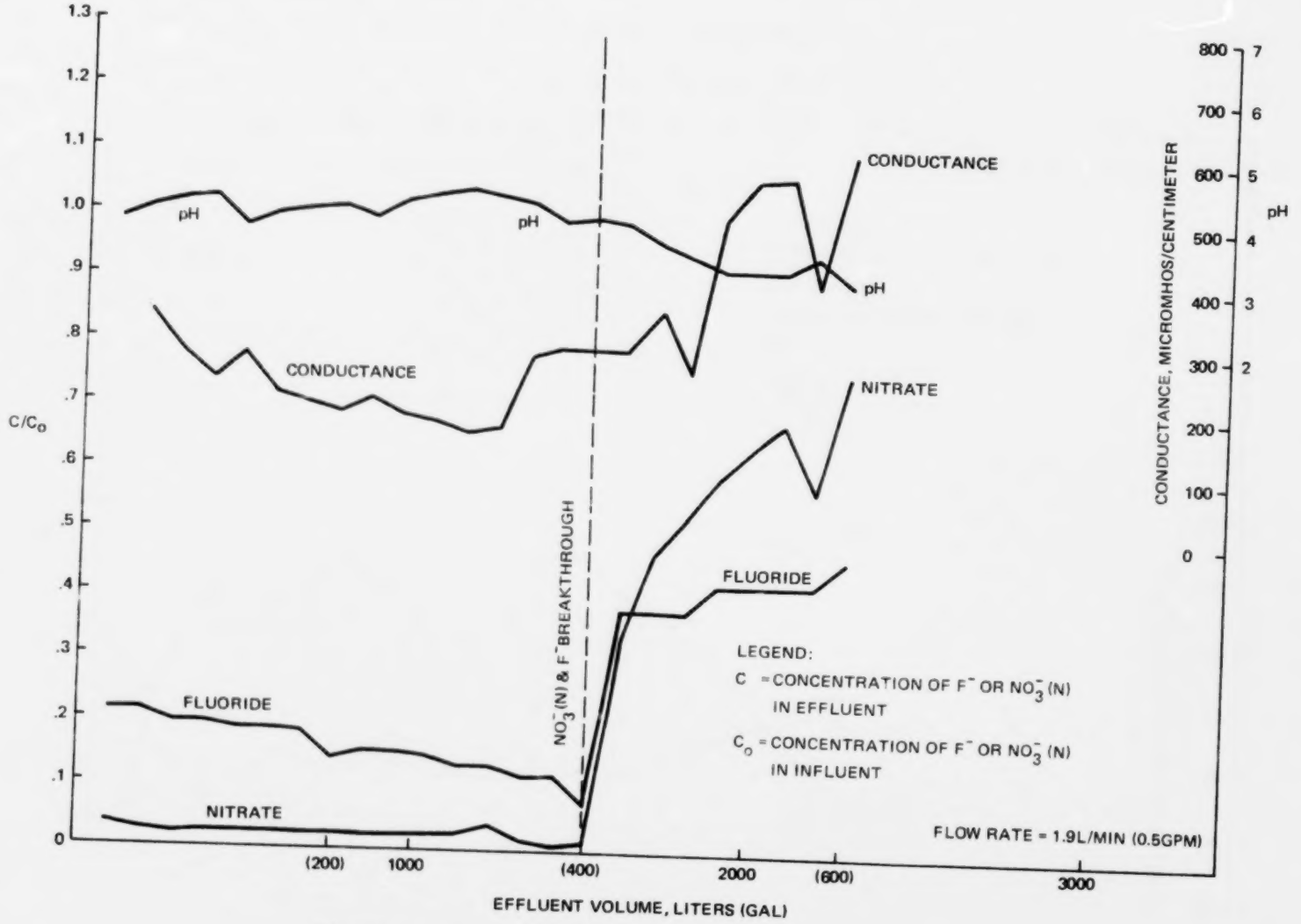

Figure 9. Ion-exchange breakthrough test no. 10.

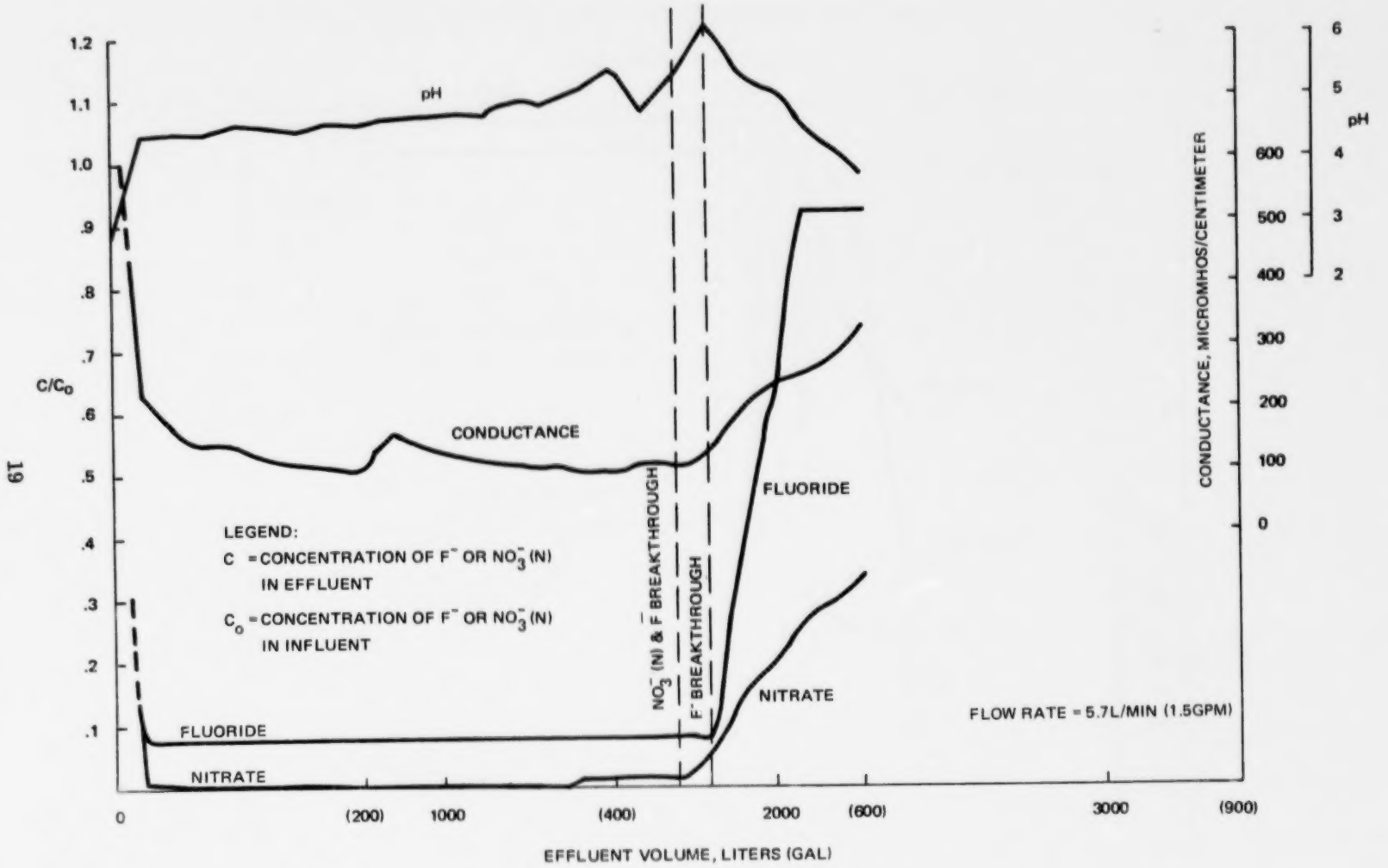

Figure 10. Ion-exchange breakthrough test no. 3.

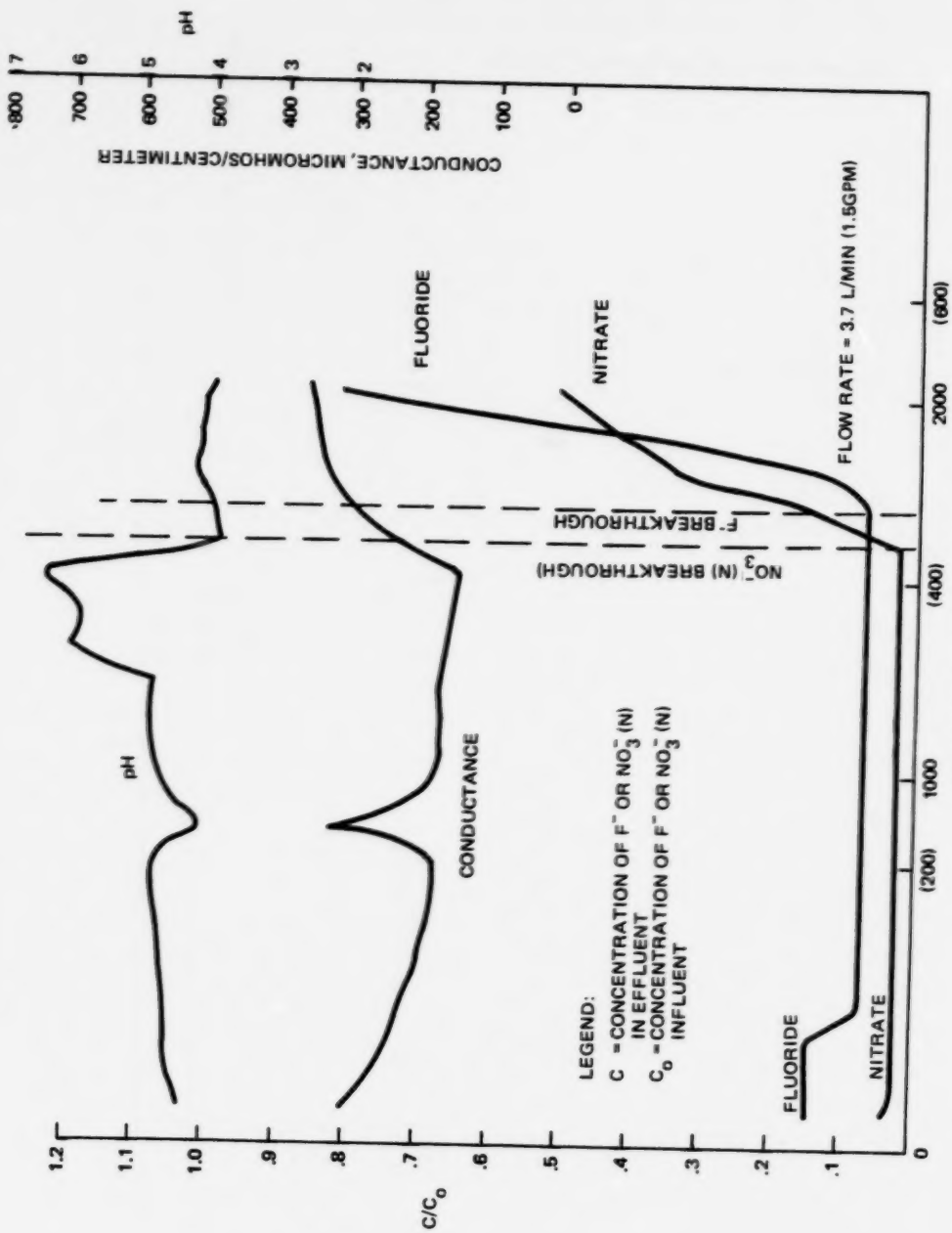

Figure 11. Ion-exchange breakthrough test no. 6.

usage, because of the tendency to increase the removal of ions deposited on the resin during the previous exhaustion (Figures 12 and 13). This regeneration condition is also necessary for effective removal of silica from the resin.

Rinse water usage following regeneration should be increased to maximize fluoride removal at the start of the next exhaustion. Insufficient rinsing causes the initial influent to complete the rinse, thus increasing fluoride leakage in the initial volume of influent (Figures 5 through 9 and 11).

pH AND HEAVY-METAL CATION CONTROL

Treatment of the rinse water with Amberlite IRA-400 ion-exchange resin increased the pH from about 3 to 10. Use of F-1 activated alumina in series with Amberlite IRA-400 resin maintained the pH at about 4 (Table 5), allowing the rinse water to be recycled in the system. Treatment of the rinse water also reduced the concentration levels of the heavy-metal cations (Table 6). As a result, build-up of these cations in the recycled rinse water is expected to be minimal.

TABLE 5. RESULTS OF RINSE WATER TREATMENT

Parameter	Influent	Effluent
pH	2 - 4	3 - 5
Conductivity, micromhos/centimeter	120 - 2000	60 - 600
Fluoride Concentration, ppm	12	1 - 3
Nitrate Concentration, ppm	60	1 - 10

TABLE 6. HEAVY METAL CATION REDUCTION

Ion	Concentration, ppm	
	Before Treatment	After Treatment
Al	0.9	3.1*
Ti	4.2	< 0.3
Cu	0.6	0.08
Fe	0.4	< 0.1

(*Increase is probably due to leaching from activated alumina)

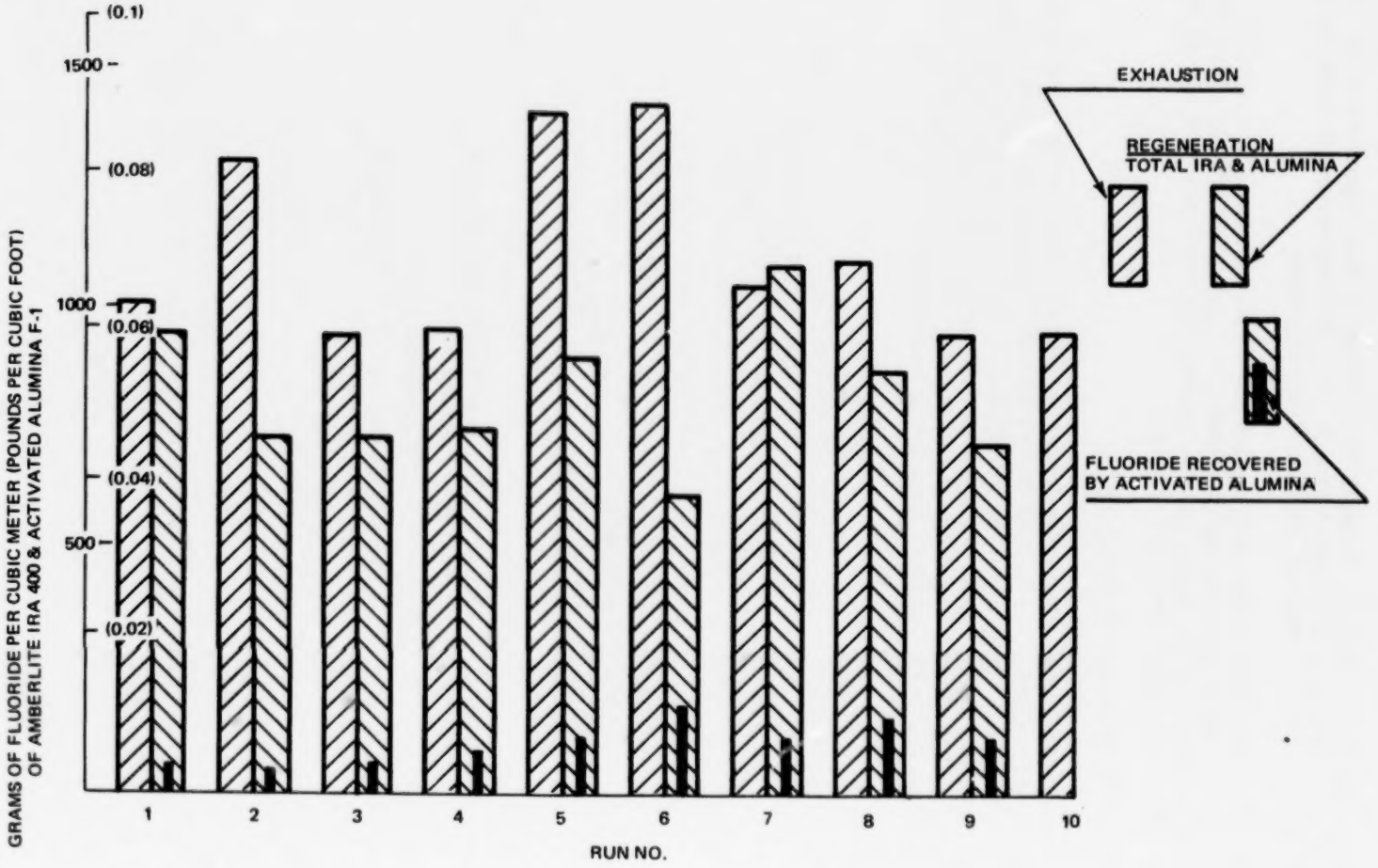

Figure 12. Ion-exchange breakthrough tests - degree of fluoride exhaustion and regeneration.

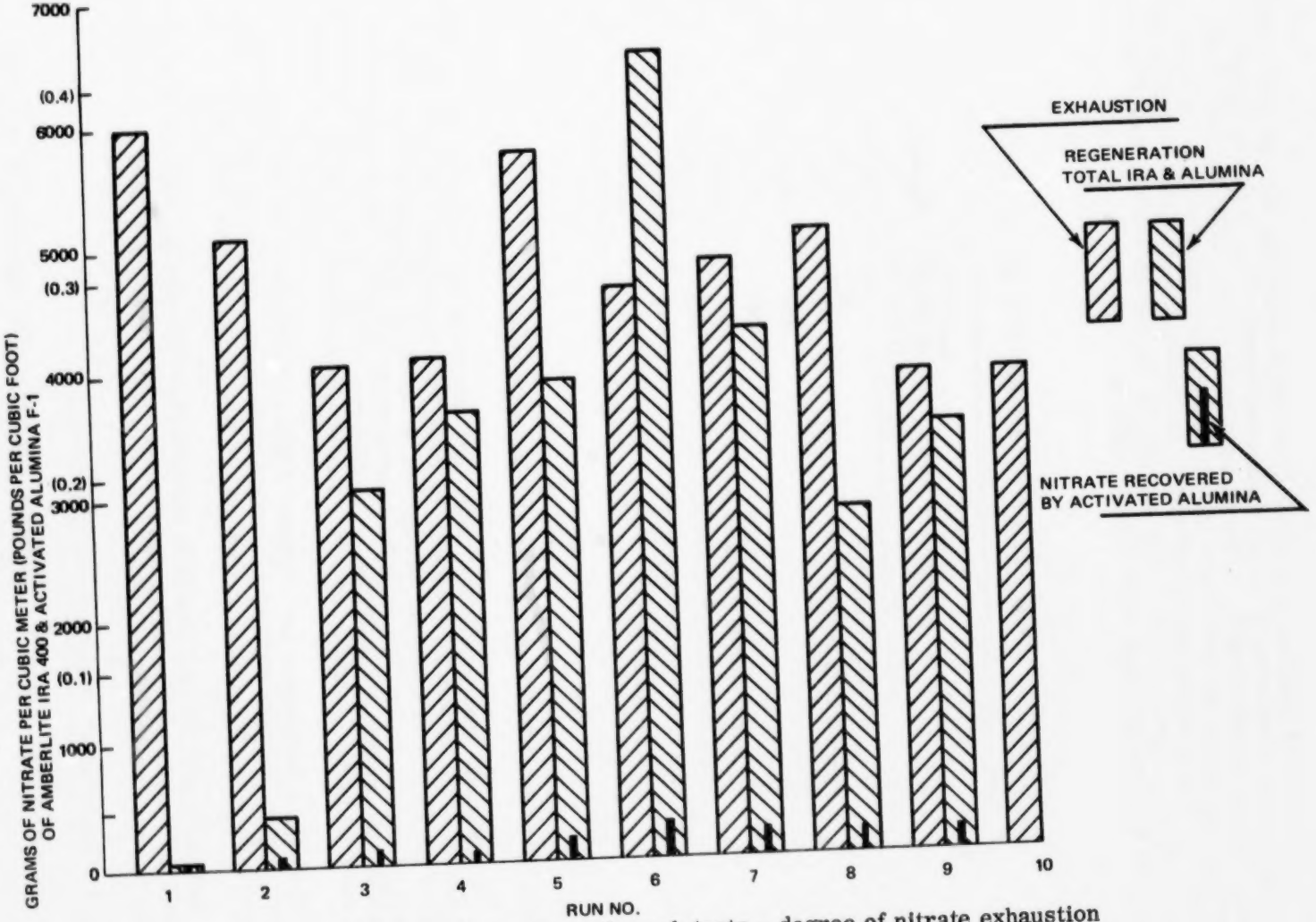

Figure 13. Ion-exchange breakthrough tests - degree of nitrate exhaustion and regeneration.

RESIN STABILITY

Physical and chemical properties of the spent Amberlite IRA-400 resin were evaluated after completion of the ten exhaustion/regeneration cycles to determine the resin stability in this system. Although significant silica fouling and slight bead breakage did occur, the total resin capacity did not decrease from the initial value (Table 7). Silica fouling can be reduced by increasing the regeneration temperature from ambient to 49°C (120°F). This increase in the regeneration temperature should also help to maintain a high breakthrough capacity.

TABLE 7. EVALUATION OF AMBERLITE IRA-400 RESIN

Property	Spent Resin, 28,320 cm^3 (1 ft^3) Test	New Resin
Moisture Holding Capacity, %	50	43 - 49
Whole Bead Content, %	77	90
Organic Fouling	None	None
Silica (SiO_2) Conc, ppm	1,146	None
Weak-Base Capacity, meq/g (dry)	0.46	0.4 (min)
Strong-Base Capacity, meq/g (dry)	3.66	3.6 (min)
Total Anion Exchange Capacity, meq/g (dry)	4.12	3.8 (min)
Fines through 50 Mesh, %	4.1	3 (max)

PRODUCTION SCALE-UP AND ECONOMIC CONSIDERATIONS

The technical base established in the pilot treatment study is sufficient to design a production-scale system for treatment of rinse waters containing about 12 ppm of fluorides and 60 ppm of nitrates. Design can be based on the maximum flow rate studied, 5.7 l/min (1.5 gpm), using the breakthrough capacity of 60,150 l (influent)/m^3 (resin) (450 gal/ft^3). Including an 80% efficiency factor, about 1.2 m^3 (42 ft^3) of resin would be needed to handle a rinse-water waste-stream of 190 l/min (50 gpm).

The capital investment for a system of this size, including two ion-exchange columns, piping, tankage and a small control system, would be about $25,000. Requirements for systems of other capacities are also presented (see Table 8).

Several system designs should be considered for the specific production operation involved to optimize the initial capital investment and the operating costs. Three possible systems are described below.

System 1 - Basic Ion-Exchange System (Figure 14)

This system is designed for a specific operation with regeneration on the off-shift.

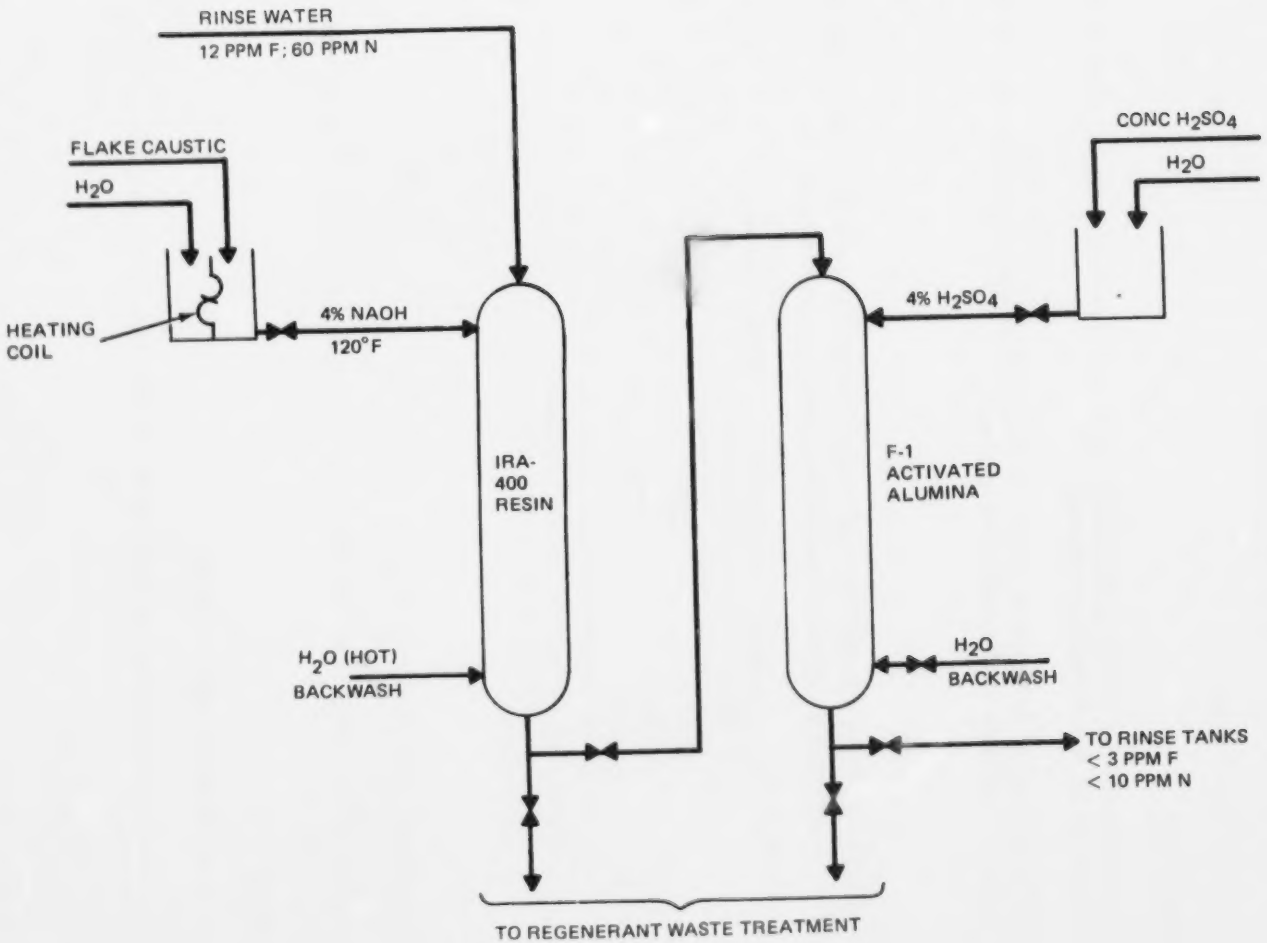

Figure 14. System 1: Basic ion-exchange system for removal of fluorides and nitrates.

Advantages

- Requires minimum capital investment
- Good for infrequent or irregular operation
- Can recycle effluent.

Disadvantages

- Resin volume may not be optimum for flow rate involved because it must be designed to fit the operating schedule
- Additional capital investment would be required to accommodate capacity increases or changes in operating schedules.

TABLE 8. CAPITAL INVESTMENTS FOR TWO-STAGE ION-EXCHANGE SYSTEMS

Rinse Water Flow Rate, l/min (gpm)	Resin Volume, m^3 (ft^3)/column	Approximate Capital Investment,* $
38(10)	0.26(9)	10,000
190(50)	1.2(42)	25,000
380(100)	2.4(84)	40,000

(*Includes two ion-exchange columns, two regenerant solution tanks, associated piping and pumps, small control system, installation and materials.)

System 2 - Surge Tank Ion-Exchange System (Figure 15)

This system incorporates a surge tank to accumulate the influent during column regeneration.

Advantages

- Permits continuous feed to system
- Requires minimum capital investment for continuous operation, especially at low flow rates
- Can recycle effluent.

Disadvantage

- Additional capital investment would be required to accommodate capacity increases or changes in operating schedules.

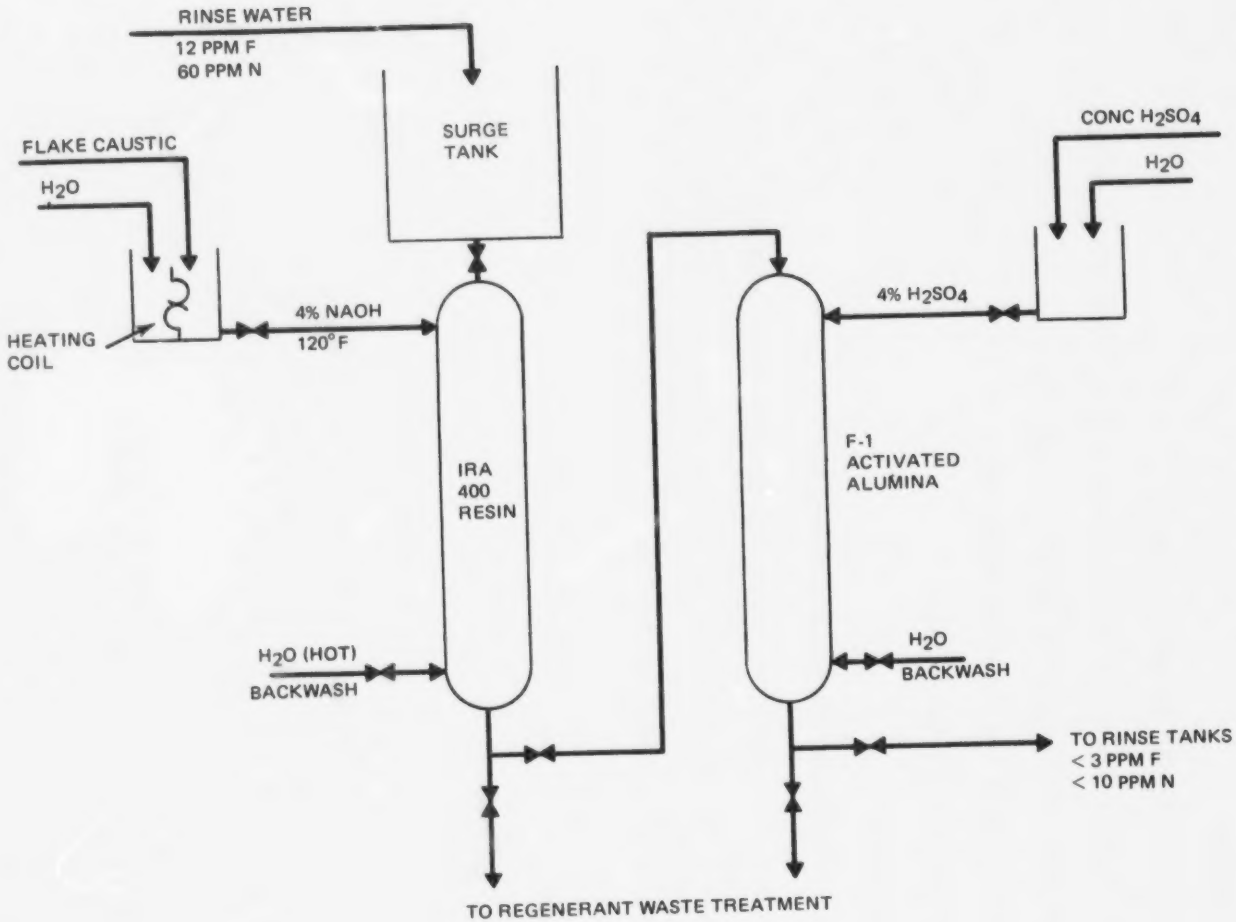

Figure 15. System 2: Surge-tank ion-exchange system for removal of fluorides and nitrates.

System 3 - Dual Ion-Exchange System (Figure 16)

This system incorporates two sets of ion-exchange columns installed so that one set can be operated while the other set is being regenerated.

Advantages

- Provides continuous operation
- Resin volume may be somewhat less than required for a single set of columns
- Capacity increase is readily available
- Minimum downtime for maintenance
- Effluent can be recycled.

Disadvantage

- Requires large capital investment.

Selection of the optimum system design depends on equipment costs (tankage versus columns), cycle length (exhaustion versus regeneration) and operating schedule. Optimization of the capital investment through system selection should be included with the other operating costs (labor, utilities, raw materials and regenerant treatment) to give a complete economic evaluation.

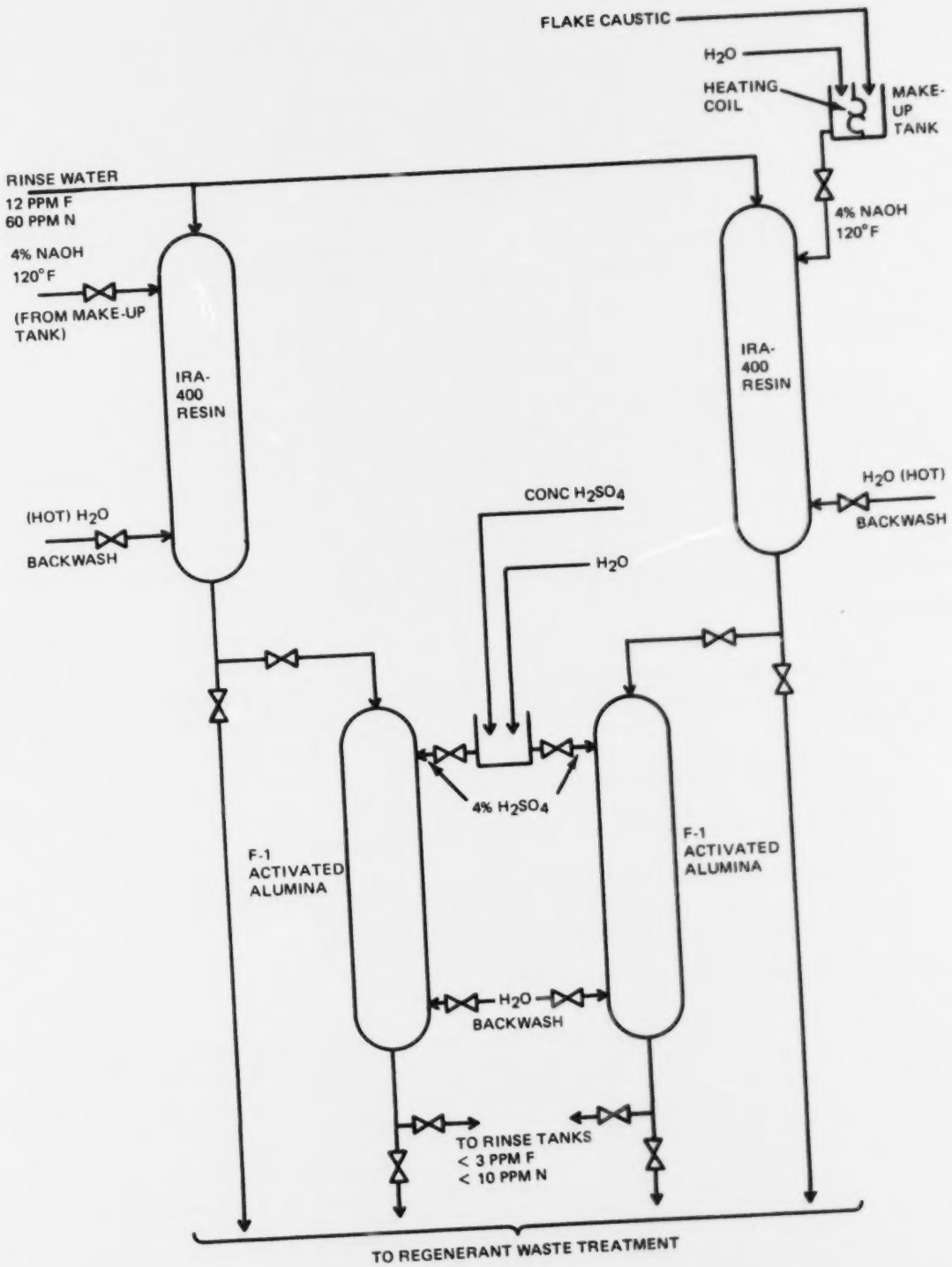

Figure 16. System 3: Dual ion-exchange system for removal of fluorides and nitrates.

SECTION 5

REMOVAL AND RE-USE OF FLUORIDES AND NITRATES FROM LIME-TREATED EFFLUENTS

APPROACH

This phase of the program was directed toward the removal and recovery of fluorides and nitrates from spent, metal-treatment acid solutions, and ion-exchange regeneration wastes in an effort to prevent ground-water pollution. The treatment approach involved lime-precipitation and solids separation of fluorides and metallic elements, mechanically aided evaporation to recover nitrates, and application of recovered nitrates as plant fertilizer. The solutions evaluated were similar to those used throughout the metalworking industry for cleaning, descaling and pretreatment (see typical industrial uses for these types of solutions in Table 9).

STUDY AREAS

The following technical efforts were involved in the development of precipitation and evaporation techniques to remove fluorides and nitrates from chemical processing solutions:

- Design of prototype treatment system
- Lime treatment and fluoride removal by centrifugation
- Removal of nitrates by evaporation from lime-treated effluents
- Use of evaporator sludge as nitrogen fertilizer.

DESIGN OF PROTOTYPE TREATMENT SYSTEM

Removal of fluorides and nitrates from spent processing solutions requires several treatment steps. A prototype treatment system (Figure 17) was designed based on studies conducted during this program. Although other system designs could be used for fluoride and nitrate removal, the system selected incorporates the treatment steps evaluated in Phases I and II of this program. Lime-treatment of various spent processing solutions requires different application levels and hold-times before separation. These treatment variations were studied in Phase I. Flocculant additions to increase solids removal were studied briefly in Phase I. Additional work is needed, however, to determine the applicability and effectiveness of this treatment step. Separation of suspended solids (calcium fluoride and metals) by centrifugation was evaluated in this study. Other solids separation techniques, such as rotary vacuum filtration or tank settling, are also feasible. Removal of dissolved solids (calcium

TABLE 9. TYPICAL INDUSTRIAL USES OF METAL-PROCESSING SOLUTIONS

Chemical Process	Pollutants Generated	Application				
		Aerospace	Automotive	Building Construction	Consumer Products	Marine
Aluminum Deoxidizer and Conversion Coating	Fluorides, Nitrates, Chromates, Heavy Metals	Skins, Fasteners, Structural Components	Trim, Decorative Coating, Painted Parts	Strip Line Coil Coating, Siding, Gutters, Storm Windows	Cans, Utensils	Superstructures, Boats, Canoes
Ferrous Alloy and Titanium Descaling	Fluorides, Nitrates, Chromates, Heavy Metals	Structural Components, Wire Cleaning	Chrome-Plated and Painted Parts, Wire	Steel Siding, I-Beam and Fence Cleaning, Wire	Ornamental Iron, Nails, Fasteners, Utensils	Hull Components, Hardware, Fasteners
Etching and Chemical Milling	Fluorides, Heavy Metals, Sulfides	Aircraft and Missile Skins, Jet Engine Parts	Printed Circuits	Pretreatment, Architectural Trim	Printed Circuits, Name Plates	Submarine Superstructures and Subcomponents
Plating	Cyanides, Fluorides, Chromates, Heavy Metals	Hard Chrome Landing Gears, Clips, Brackets, Heat-Treated Parts	Bumpers, Hub Caps, Trim, Knobs, Handles	Heavy Equipment, Nails, Bolts, Hardware	Costume Jewelry, Appliances, Bicycles, Lamps, Tools, TV's, Radios,	Engine Parts. Cleats, Hardware, Trim

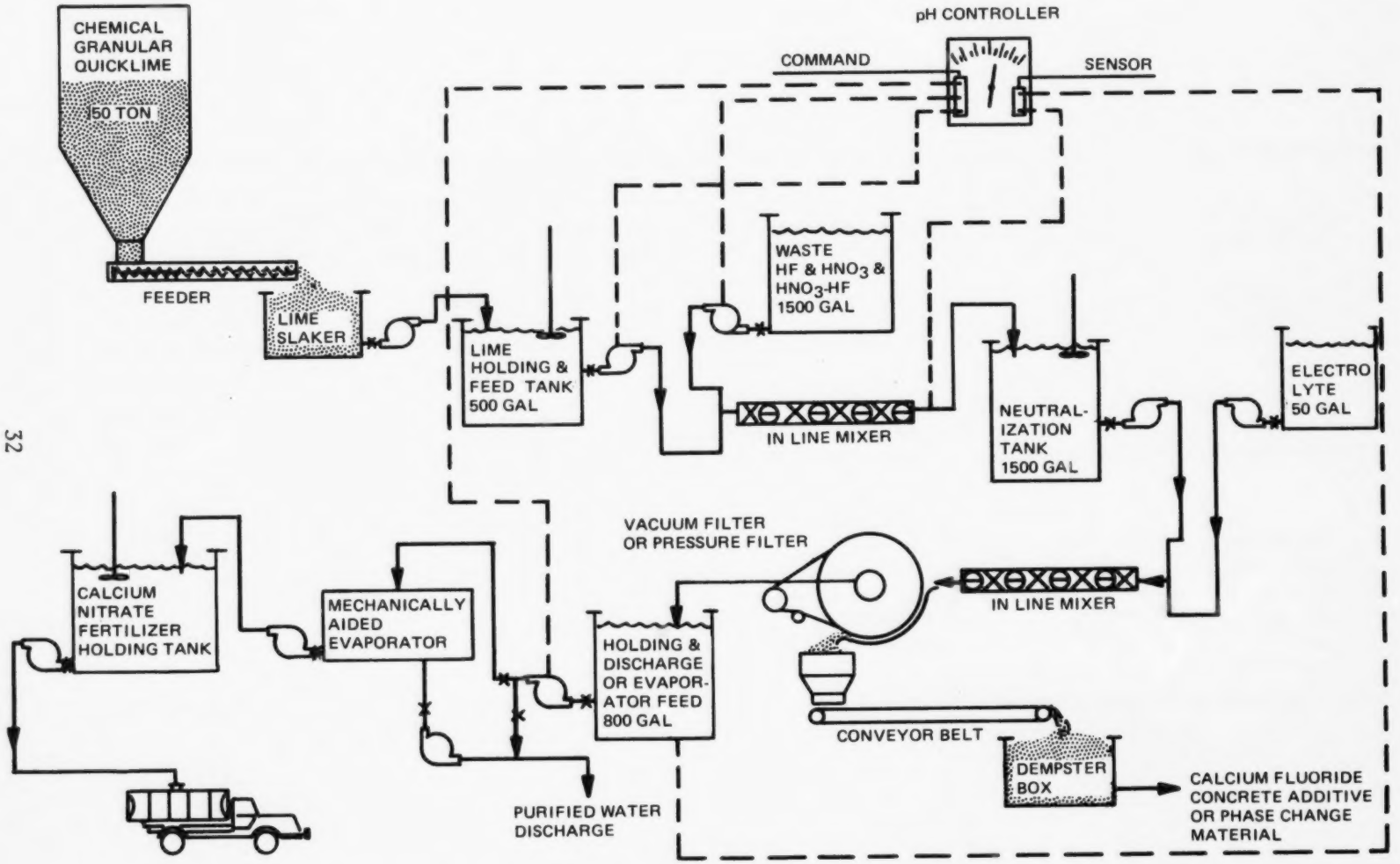

Figure 17. Prototype fluoride and nitrate waste treatment system.

nitrate) from the centrate by mechanically aided evaporation was studied in Phase II. The calcium nitrate evaporator sludge was evaluated for use as a nitrate fertilizer in an effort to reduce disposal costs and provide some return on material costs.

LIME TREATMENT AND FLUORIDE REMOVAL BY CENTRIFUGATION

The lime treatment and centrifugation techniques developed in the initial program were used to generate test material for the pilot evaporator studies from titanium descaling, Amchem 7-17 deoxidizer, Alodine aluminum conversion coating and ion-exchange regeneration waste solutions (Table 10).

Pilot Centrifuge Setup and Calibration

A Sharples/Fletcher Mark III centrifuge (Figure 18) manufactured by the Pennwalt Corporation was used for all laboratory pilot testing. This centrifuge, which has a 35.6 cm (14 in)-diameter by 15.2 cm (6 in)-high basket and a speed capability of 3250 rpm, is designed for separation studies and performance analyses to generate data for projected production equipment. The pilot centrifuge system consists of the following components:

- 208-l (55-gal) tank with Lightnin AG-100 air-powered mixer for making up lime slurry
- Vanton PY-60 centrifugal pump to transfer lime to treatment tank
- Treatment tank with Holloway Super electric mixer and Jabsco P-6 centrifugal feed pump
- 114-l (30-gal) polyvinyl chloride rectangular tank to receive treated effluent (at rear of centrifuge)
- 208-l (55-gal) drum to receive sludge skimmed from centrifuge bowl

The Sharples/Fletcher Mark III centrifuge is completely variable in speed over the 0-3250 rpm range. The Sharples division of the Pennwalt Corporation recommended that testing be conducted at a force of 1300G and flow rates of up to 3.8 l/min (1.0 gpm). The centrifuge speed necessary to obtain the 1300G force was calculated as follows:

Centrifugal force in multiples of the force of gravity

$$= (5.59 \times 10^{-4}) \text{ (Bowl speed in rpm)}^2 \text{ (Bowl diameter in centimeters)}$$

$$= (1.42 \times 10^{-5}) \text{ (Bowl speed in rpm)}^2 \text{ (Bowl diameter in inches)}$$

Bowl speed = 2550 rpm

Bowl diameter = 35.6 cm (14 in)

TABLE 10. COMPOSITION AND USES OF FLUORIDE AND NITRATE-CONTAINING PROCESSING SOLUTIONS

Nitrate/Fluoride-Containing Process Solutions - Typical Formulations	Typical Uses	Manufacturer
Aluminum Deoxidizer Solution **18-56g/l** AMCHEM (2-6 oz./gal.) 7-17 deoxidizer (contains potassium dichromate and fluoride salts) 10-20% volume nitric acid 1.4 kg/l (42° Baume)	Cleaning of aluminum parts prior to: • Conversion coating (Alodine) • Masking of parts for chemical milling • Spot welding	AMCHEM Products Inc., Ambler, Pa.
Titanium Descaling Solution 35-45% volume nitric acid 1.4 kg/l (42° Baume) Actane #70 1.5-3% by weight or Hydrofluoric acid 1.5-3% by volume, using 70% weight acid	Cleaning of titanium parts for: • Welding • Removal of heat-treat scale • Painting	Chemical grade acids (sources open) Actane #70 - Enthone Inc., West Haven, Connecticut
Aluminum Conversion Coating Solution (Alodine). Alodine contains chromic acid and complex fluoride salts.	Used to produce a protective coating on aluminum to: • Increase corrosion resistance • Increase paint adhesion	AMCHEM Products, Inc., Ambler, Pa.
Ion-exchange regeneration waste H_2SO_4 regeneration waste NaOH regeneration waste	Regeneration of: Activated alumina IRA 400 used to treat process rinse waters	In-house

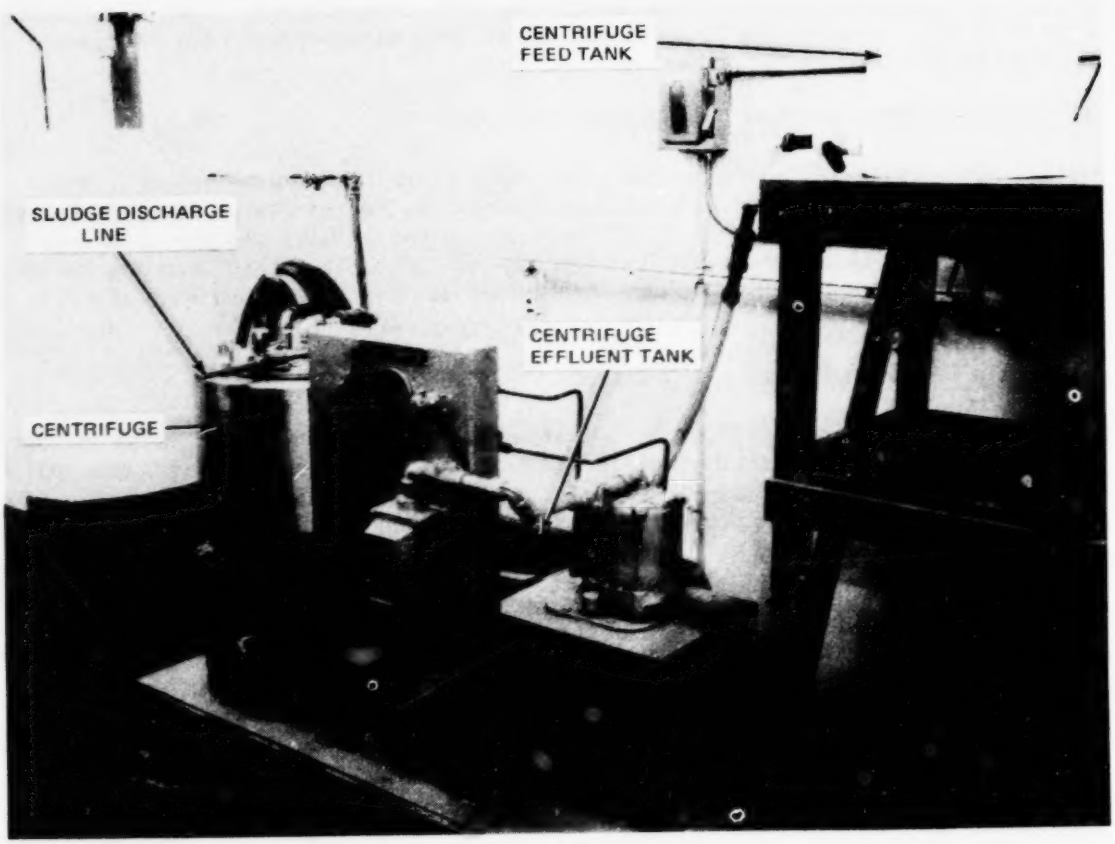

Figure 18. Pilot centrifuge system for removal of calcium fluoride from lime-treated process solutions.

Lime Slaking

Chemical granular quicklime, which was found to provide optimum fluoride and metal ion removal from the solutions studied in the initial program, was used for all tests in this program. A slurry concentration of 0.24 kg lime/l water (20.3 lb lime/gal water) was used for all process solution pilot testing. Dry, chemical granular quicklime was added to the ion-exchange regeneration solution because of its low fluoride and nitrate concentrations, 73 and 650 ppm, respectively. The lime slaking time of 25 to 30 minutes gave a 49°C (120°F) solution temperature rise above ambient temperature.

Titanium Descaling Solution Treatment

Eighty-seven-l (23-gal) batches of titanium descaling solution having fluoride and nitrate concentrations of 117,000 and 64,000 ppm, respectively, were treated with 123 l (32.5 gal) of lime slurry. After the lime-treated solution was mixed for one hour, its pH was 10.2 and its temperature was 82°C (180°F). After standing for 18 hours, the lime-treated solution was again mixed and fed to the centrifuge at a rate of 1.9 l/min (0.5 gpm).

Aluminum Deoxidizer Solution Treatment

The concentrations of fluoride, nitrate and hexavalent chromium in the untreated, Amchem 7-17 aluminum deoxidizer solution were 1,500, 26,000 and 5,500 ppm, respectively. To reduce the hexavalent chromium to trivalent chromium, 2.3 kg (5 lb) of sodium metabisulphite were added to 114 l (30 gal) of the Amchem 7-17 solution. After 64 l (17 gal) of lime slurry were added, the solution was mixed for one hour and allowed to stand for 18 hours. The treated solution was again mixed and fed to the centrifuge at a rate of 1.9 l/min (0.5 gpm).

Aluminum Conversion Coating Solution Treatment

Alodine 600 aluminum conversion coating solution was treated in conjunction with Amchem 7-17 aluminum deoxidizer solution because of its low nitrate (N) concentration (250 ppm) and its infrequent dumping (once per year). A mixture of 28.4 l (7.5 gal) of Alodine 600 solution and 28.4 l (7.5 gal) of Amchem 7-17 solution was treated with 1.1 kg (2.5 lb) of sodium metabisulphite to reduce the hexavalent chromium (3,000 ppm) to trivalent chromium. Complex fluorides (e.g., BF_4^- fluoborates) contained in the Alodine 600 solution were decomplexed by adding 700 g (1.5 lb) of aluminum sulfate. Previous experiments had shown that 12 g aluminum sulfate/l solution (0.1 lb/gal) would dissociate 300 ppm of fluoride (F^-) from the fluoborate (BF_4^-). The Alodine 600/Amchem 7-17 mixture was mixed for one-half hour and allowed to stand for 18 hours. Addition of 32.2 l (8.5 gal) of lime slurry to the mixture brought the pH to 11.5. The mixture was then agitated for one hour and allowed to settle for 18 hours. After the treated solution was mixed for one minute, it was centrifuged at a rate of 1.9 l/min (0.5 gpm).

Ion-Exchange Regeneration Waste Treatment

A mixture of various regenerant solutions from the ion-exchange tests was treated. This 1.3 pH mixture, which consisted of 30.3 l (8 gal) of sulfuric acid

TABLE 11. LIME-TREATMENT RESULTS FOR CHEMICAL PROCESSING SOLUTIONS AND ION-EXCHANGE REGENERANT

Solution	Initial Concentration, ppm (F)	(N)	Solution-To-Slurry* Ratio	Temp. Rise During Treatment, °C (°F)	Effluent pH	Effluent Concentration, ppm (F)	(N)	Dissolved Solids After Fluoride Removal, %
$HF-HNO_3$ Descaling	117,000	64,000	1:1.4	38 (100)	10.2	3	28,000	14.9
AMCHEM 7-17 Aluminum Deoxidizer	1,500	26,000	1:0.6	10 (50)	11.5	3	19,000	11.4
AMCHEM 7-17 Aluminum Deoxidizer & Alodine 600	2,000	34,500	1:0.6	10 (50)	11.5	3	23,000	14.1
Ion-Exchange Regeneration Waste	73	600	100 Grams/ Liter (Dry)	–	12.7	5	600	3.3

*Slurry: 0.24 kg CaO/l (2.0 lb/gal.)

regenerant and 15.1 l (4 gal) of sodium hydroxide regenerant, had fluoride and nitrate concentrations of 73 and 600 ppm, respectively. Addition of 4.5 kg (10 lb) of dry calcium oxide (CaO) to the solution mixture raised the pH to 12.7 after being mixed for one hour. After standing for 24 hours, the mixture was centrifuged at a rate of 1.9/min (0.5 gpm).

Summary of Results

The results obtained when calcium oxide (chemical granular quicklime) was used to treat three chemical processing solutions and an ion-exchange regeneration waste are summarized (Table 11). These tests showed that treatment of titanium descaling solution, aluminium deoxidizer solution and ion-exchange regeneration waste with lime removes fluorides and dissolved metallic constituents to give an effluent having a fluoride concentration of 3 to 5 ppm. The Alodine 600 aluminum conversion coating/aluminum deoxidizer solution required preliminary treatment with aluminum sulfate to decomplex the fluoborates. Secondary treatment of this solution with lime slurry removed dissolved metals and produced an effluent having a fluoride concentration of 5 ppm.

The lime-treated effluents with their resultant fluoride and nitrate levels (Table 11) were used as feed solutions for mechanically aided evaporation tests. After mechanically aided evaporation, final effluents containing less than 1 ppm of fluorides and 5 ppm of nitrates were produced (see Table 12).

REMOVAL OF NITRATES FROM LIME-TREATED EFFLUENTS

Background

Lime-treatment and centrifugation of fluoride and nitrate waste solutions removes calcium fluoride but leaves calcium nitrate in solution. Separation of calcium nitrate from solution by evaporation produces discharge water with less than 5 ppm of nitrates and a concentrated calcium nitrate solution (heavy liquid) that can be used as a plant fertilizer. Pilot testing showed that separation of nitrates by evaporation is feasible for waste solutions containing 600 to 28,000 ppm of nitrates (N) or 3 to 15% of solids after lime treatment. Four solutions (Table 11) were studied in this phase of the program.

Equipment

A Rototherm evaporation system (Figure 19) supplied by Artisan Industries, Inc., Waltham, Massachusetts, was used for the pilot tests. The Rototherm E unit is a thin-film, mechanically aided evaporator with a ribbon blade rotor. A 0.12-m^2 (1.31-ft^2) rising film pre-evaporator feeds the 0.09-m^2 (1.0-ft^2) Rototherm unit. Vapors are condensed in a 0.95-m^2 (10.2-ft^2) shell-and-tube condenser. This type of evaporator was selected because it can handle thick liquors more effectively than other types. Countercurrent flow (Figure 20) was used throughout the system. Feed rate was controlled by a Gearchem Model G4-ACK-KKA gear pump (Figure 21) supplied by the Eco Pump Corporation, South Plainfield, New Jersey. This positive-displacement pump provided excellent feed rate control without any mechanical difficulties during pilot testing. An upstream filter was used to prevent pump damage.

TABLE 12. ROTOTHERM EVAPORATOR SYSTEM - PILOT EVALUATION AT GRUMMAN FACILITIES (EVAPORATOR OPERATED WITH AMBIENT-TEMPERATURE FEED)

Solution	Test No.	Feed Conc, ppm N	Feed Rate, kg/hr (lb/hr)	Rototherm Steam Temp, °C(°F)	Evaporation Capacity, kg/hr (lb/hr)	Steam Economy, kg evap/kg steam	Evap Level, %	Distillate Concentration ppm N	Distillate Concentration ppm F	Bottoms Concentration, ppm N
$Ca(NO_3)_2$	1	27200	17.2(37.9)	133(272)	12.1(26.6)	81.8	70.2	4.2		140000
Standard	2	27200	13.4(29.5)	162(323)	9.7(21.3)	76.6	72.2	2.6		128000
Test Solution	3	27200	13.1(28.9)	167(332)	10.0(22.0)	76.9	76.1	3.1		140000
HNO_3–HF	4	28000	16.3(36.0)	113(235)	10.3(22.6)	81.6	62.7	1.0	< 1	115600
Titanium	5	28000	15.6(34.3)	114(237)	10.6(23.3)	82.6	67.9	1.3	< 1	150300
Descaling	6	28000	15.6(34.4)	114(237)	9.7(21.4)	80.8	62.2	0.7	< 1	168900
Solution	7	28000	16.6(36.5)	111(232)	9.9(21.8)	80.7	59.5	0.3	< 1	135400
AMCHEM 7-17	8	19000	13.7(30.2)	169(336)	11.5(25.3)	78.3	83.8	2.6	< 1	197000
Aluminum	9	19000	14.1(31.1)	164(327)	10.5(23.2)	81.1	74.6	1.0	< 1	233000
Deoxidizer	10	19000	13.9(30.7)	149(301)	10.0(22.1)	77.8	72.0	0.8	< 1	233000
Solution	11	19000	15.5(34.1)	132(270)	10.5(23.1)	79.7	67.7	0.8	< 1	191000
	12	19000	17.8(39.1)	119(247)	10.4(23.0)	77.7	58.8	0.8	< 1	110000
	13	19000	14.5(31.9)	131(268)	10.4(23.0)	80.9	71.5	1.0	< 1	164000
Alodine 600	14	23000	13.2(29.1)	151(303)	9.7(21.4)	79.3	73.5	2.0	< 1	203000
Aluminum	15	23000	13.4(29.5)	154(310)	9.8(21.5)	78.8	72.8	3.8	< 1	204000
Conversion Coating Solution & AMCHEM 7-17 Deoxidizer	16	23000	13.4(29.5)	149(300)	9.0(19.8)	76.4	66.9	2.7	< 1	222000
Ion-Exchange	17	600	12.2(26.8)	167(332)	11.8(26.0)	80.0	96.8	0.2	< 1	–
Regeneration	18	600	11.8(25.9)	149(300)	10.2(22.5)	80.4	87.1	0.1	< 1	36000
Waste	19	600	10.0(22.0)	133(272)	8.4(19.4)	81.4	83.4	0.1	< 1	34000

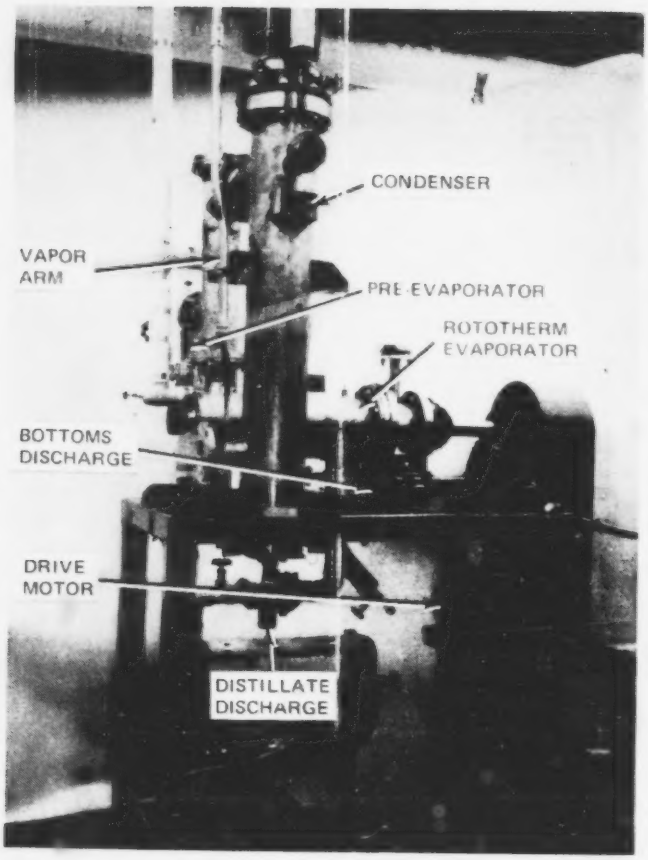

Figure 19. Rototherm evaporator system for concentration of calcium nitrate in lime-treated process solutions.

A steam generator (Figure 22) was used because high-pressure steam was not available at the laboratory test site. The Grumman and Artisan pilot testing facilities were equivalent.

Operating Parameters

Both feed rate and steam pressure were varied during pilot evaluation of the Rototherm evaporation system. Feed rates ranged from 9.1 to 36.3 kg/hr (20 to 80 lb/hr). In the preliminary pilot tests performed at the Artisan facilities, the feed was preheated to 99-103°C (210-217°F) before it was allowed to enter the pre-evaporator. In the Grumman pilot tests, the feed remained at ambient temperature. Process steam was introduced at pressures up to 900 kPa (130 psi absolute). The evaporation system itself was operated at atmospheric pressure.

Test Procedure

The Rototherm evaporation system was used to determine whether lime-treated waste solutions could be separated to give a liquid with less than 10 ppm nitrate (N) and a sludge that could be used as a plant fertilizer. The effect of feed rate and steam pressure on bottoms concentration, steam use and evaporation level was studied. Several lime-treated processing solutions having nitrate concentrations ranging from 19,000 to 28,000 ppm and an ion-exchange regeneration waste containing 600 ppm of nitrate (N) were used. The distillate in each test contained less than 5 ppm of nitrate (N). The solutions had been treated with different lime concentrations to account for variations in their initial fluoride and nitrate concentrations (see Table 11).

Evaporation to a point just before bottoms crystallization is desirable, because this minimizes fertilizer shipping costs without creating significant evaporator fouling. The feed rate for each test was adjusted to provide a reasonable bottoms concentration (i.e., heavy liquid without crystallization) averaging about 50% solids. The nitrogen content in the solids is comparable to that found in nitrate fertilizers (about 15%). The metals concentrations in the sludge were also comparable to those occurring in commercial calcium nitrate (Table 13). Use of this byproduct as a plant fertilizer was shown to be effective in tests performed at the Long Island Vegetable Research Farm of Cornell University, Riverhead, New York. (See Section 5, Use of Evaporator Sludge as Nitrogen Fertilizer, and Appendix D.)

Artisan Pilot Tests

Preliminary testing of the Rototherm evaporation system was performed at the pilot facilities of Artisan, Inc., Waltham, Massachusetts, to determine the feasibility of using this system and to establish initial operating conditions for further testing. Lime-treated, nitric-hydrofluric acid titanium descaling solution was used in these tests. An evaporation level of 70% was required to concentrate the 15% solids feed to 50% solids sludge. The feed was preheated to 100°C (212°F) for each of the tests. Although the distillates contained up to 50 ppm of nitrates (N), the Grumman pilot tests showed that nitrate levels less than 5 ppm (N) could be obtained consistently with this system (see test results and temperature profiles in Tables 14 and 15, respectively).

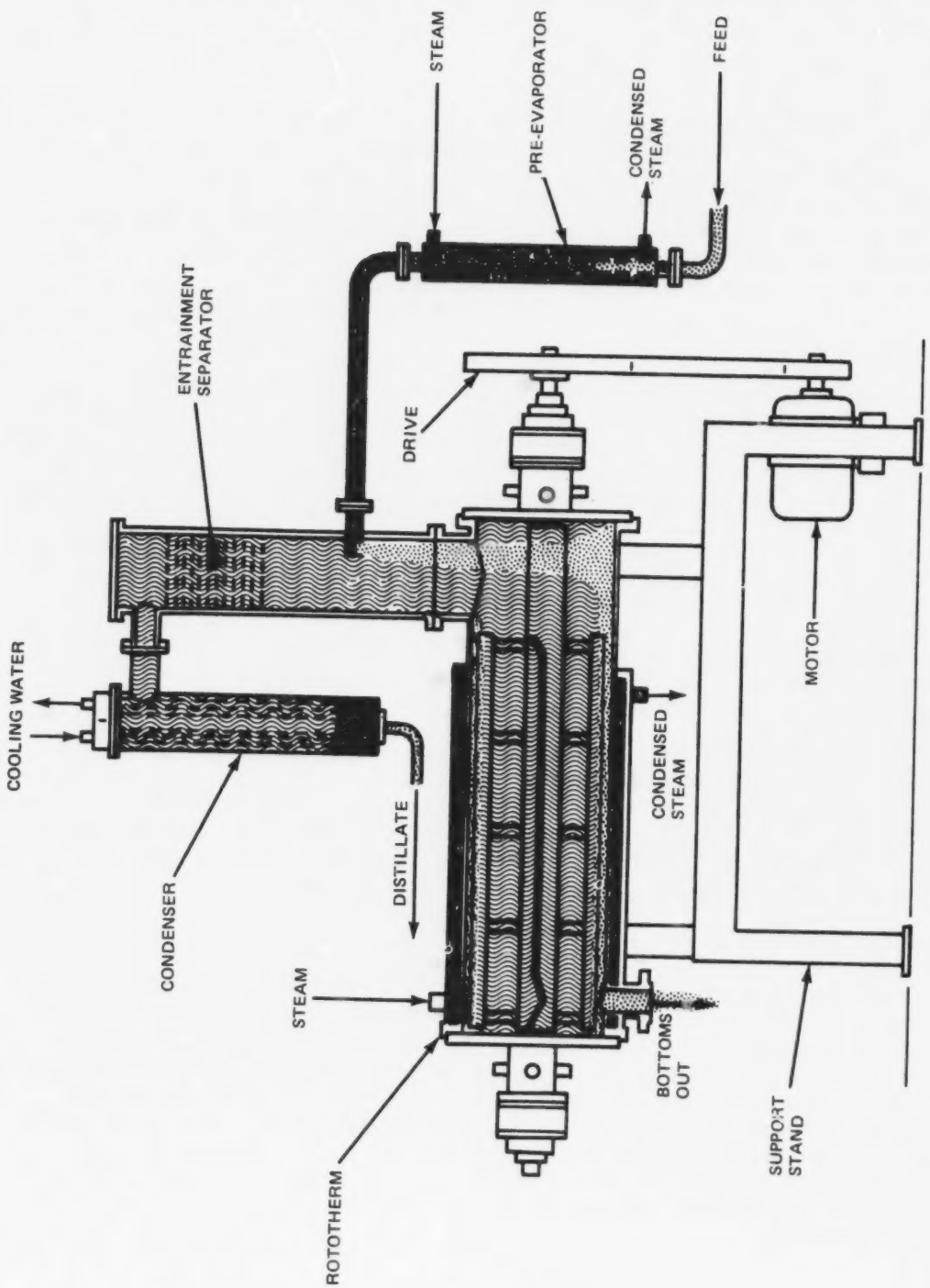

Figure 20. Countercurrent flow in Rototherm evaporator system.

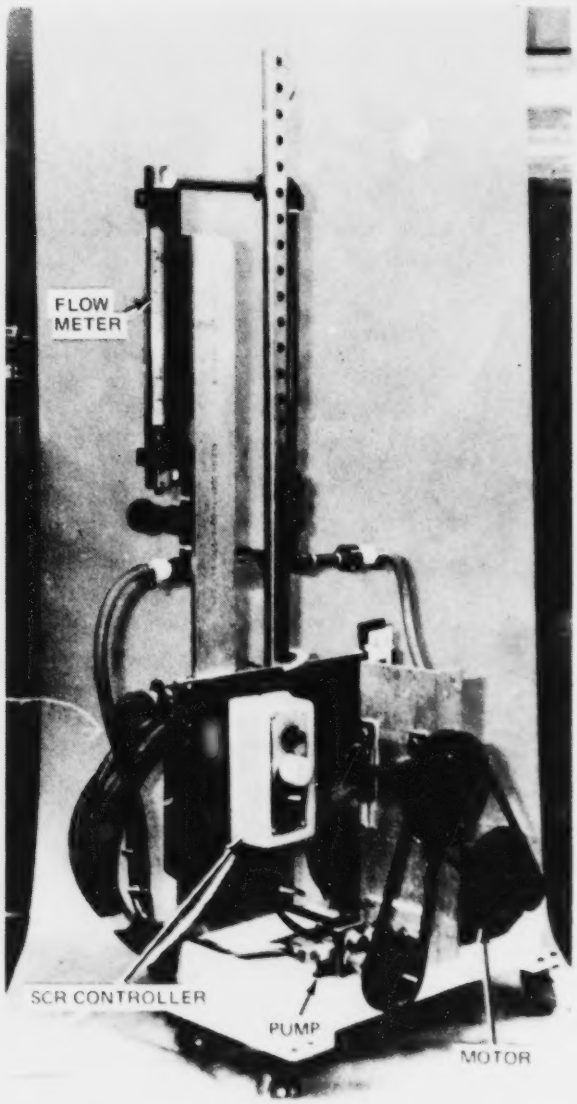

Figure 21. Gearchem pump used with pilot evaporation system.

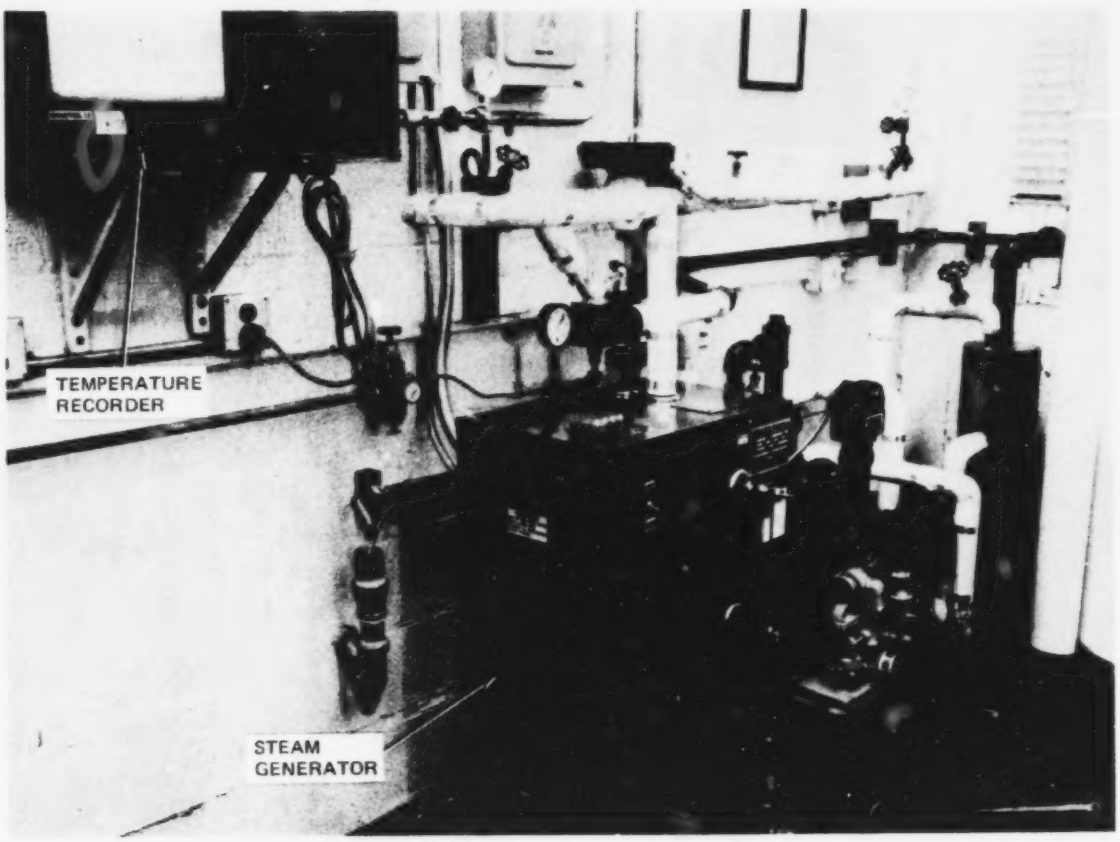

Figure 22. Steam generator used with pilot evaporation system.

TABLE 13. CALCIUM NITRATE IMPURITIES DETERMINED BY OPTICAL EMISSION SPECTROSCOPY

Calcium Nitrate	Composition, %							
$Ca(NO_3)_2$ Source	Na	Ti	V	Al	Sn	Mn	Cu	Fe
Aluminum Deoxidizer Sludge (13.6%N; 55.6% Solids)	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
HNO_3 – HF Descale Sludge (17.4%N; 62.5% Solids)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Commercial $Ca(NO_3)_2$	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Artisan Pilot Test Sludge	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Reagent Grade $Ca(NO_3)_2$	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

TABLE 14. ROTOTHERM EVAPORATOR SYSTEM - PILOT EVALUATION AT ARTISAN FACILITIES (HF-HNO_3 TITANIUM DESCALING SOLUTION PREHEATED (100°C/212°F) FEED)

Test No.	Feed Rate, kg/hr (lb/hr)	Pre-Evaporator Steam Temp, °C(°F)	Rototherm Steam Temp, °C(°F)	Evaporation Capacity, kg/hr (lb/hr)	Steam Economy, (kg evap/kg steam)	Evap Level, %	Distillate Concentration, ppm N
1	17.3(38.2)	144(291)	102(215)	11.4(25.2)	100	66.0	12
2	20.6(45.3)	144(291)	102(215)	12.8(28.1)	100	62.3	30
3	29.3(64.6)	143(290)	102(216)	13.2(29.0)	99.7	44.8	26
4	24.1(53.0)	150(302)	103(217)	14.5932.0)	99.4	60.5	22
5	22.7(50.0)	154(309)	103(217)	14.9(32.8)	99.4	65.7	21
6	28.4(62.5)	142(287)	122(252)	17.2(37.8)	96.7	60.5	24
7	28.1(61.8)	140(284)	138(280)	19.7(43.5)	94.6	70.4	17
8	27.8(61.2)	140(284)	158(317)	20.6(45.4)	90.7	74.4	12
9	23.5(51.7)	140(284)	163(326)	20.4(44.9)	90.4	86.7	25
10	35.7(78.7)	158(317)	–	17.7(38.9)	94.2	49.4	52
11	34.3(75.6)	157(315)	163(326)	26.5(58.3)	90.5	77.3	36
12	29.5(65.0)	157(314)	176(348)	24.7(54.4)	89.5	83.6	52
13	26.8(59.0)	158(316)	173(344)	22.2(49.0)	89.1	83.0	30
14	22.4(49.3)	158(316)	174(345)	17.8(39.1)	88.0	79.3	15
15	9.9(21.8)	–	175(347)	8.5(18.8)	89.1	86.2	2

Pre-Evaporator Evaluation

To test the pre-evaporator, the system was started up without turning on the Rototherm rotor. The pre-evaporator steam was run at 143-154°C (290-310°F) with feed rates of 17.2-29.5 kg/hr (38-65 lb/hr). Evaporation levels of 45 to 66% were achieved at a steam economy of 99% (Table 14, Tests 1-5 and 10). To achieve the evaporation level desired (about 70%), the feed rate would have to be reduced below 17.2 kg/hr (38 lb/hr) using the pre-evaporator only.

Rototherm Evaluation

Evaluation of the Rototherm evaporation system was accomplished using steam temperatures of 121-177°C (250-350°F) at feed rates of 22.7-34.0 kg/hr (50-75 lb/hr). In this case, evaporation levels ranged from 60 to 87%. More than 70% evaporation (Table 14, Tests 7-9 and 11-14) was obtained at steam temperatures above 138°C (280°F). Optimum operating conditions were found to be those of Test 11 (Table 14) in which 77% evaporation was achieved at 34.3 kg/hr (75.6 lb/hr) of feed. This required a steam pressure of 690 kPa (100 psi absolute).

Grumman Pilot Tests

Pilot testing of the Rototherm evaporation system was completed at Grumman's test facility using a rented unit. The Rototherm evaporator system was set up in conjunction with the centrifugal treatment system described previously. Tests were conducted on a standard calcium nitrate solution prepared from commercial calcium nitrate, as well as on three process solutions (Table 11) and the ion-ex-change regeneration waste solution. Ambient-temperature feed was used for each of these tests. Test results and temperature profiles are presented (see Tables 12 and 16, respectively).

Standard Calcium Nitrate Solution

Feed rates of 12.7 to 17.2 kg/hr (28 to 38 lb/hr) were tested at steam temperatures of 133-167°C (272-332°F). The 70-76% evaporation levels that were achieved (Tests 1-3, Table 12) were sufficient to concentrate the 15% solids feed to 50% solids in the bottoms.

Titanium Descaling Solution

In these tests, a low evaporation level (59 to 68%) was obtained because the steam temperature was too low (113°C/235°F) and the feed rate too high (15.4-16.8 kg/hr or 34-37 lb/hr) to concentrate the solids from 15 to 50% (Table 12, Tests 4-7).

Aluminum Deoxidizer Solution

An acceptable evaporation level (greater than 75% for the 11% solids feed) was obtained in these tests (Table 12, Tests 8-9) at the higher steam temperatures (164-168°C/327-335°F) for feed rates of 13.6-14.5 kg/hr (30-32 lb/hr). Tests at higher feed rates (15.4-17.7 kg/hr or 34-39 lb/hr, Tests 11-12, Table 12) and lower steam temperatures (121-149°C/250-300°F, Table 12, Tests 10-13) gave low evaporation levels (58 to 72%).

TABLE 15. OPERATING TEMPERATURES - ROTOTHERM EVAPORATOR SYSTEM - PILOT EVALUATION AT ARTISAN FACILITIES ($HF-HNO_3$ TITANIUM DESCALING SOLUTION)

Test No.	Temp, °C(°F)				
	Feed	Distillate	Bottoms	Pre-Evaporator Steam	Rototherm Steam
1	99(211)	103(218)	94(201)	144(291)	102(215)
2	100(212)	106(223)	96(204)	144(291)	102(215)
3	101(213)	104(220)	101(214)	143(290)	102(216)
4	101(213)	106(223)	104(220)	150(302)	103(217)
5	101(213)	109(229)	107(225)	154(309)	103(217)
6	101(213)	104(219)	107(224)	142(287)	122(280)
7	101(213)	106(222)	104(219)	140(284)	138(280)
8	101(213)	104(220)	143(290)	140(284)	158(317)
9	101(213)	116(240)	142(288)	140(284)	163(326)
10	103(217)	102(216)	98(208)	158(317)	–
11	102(216)	106(222)	145(293)	157(315)	163(326)
12	103(217)	108(226)	147(296)	157(314)	176(348)
13	102(215)	112(234)	146(295)	158(316)	173(344)
14	102(215)	132(270)	147(296)	158(316)	174(345)
15	101(214)	101(214)	145(293)	–	175(347)

TABLE 16. OPERATING TEMPERATURES - ROTOTHERM EVAPORATOR SYSTEM - PILOT EVALUATION AT GRUMMAN FACILITIES

Solution	Test No.	Temp, °C(°F) Feed	Distillate	Bottoms	Pre-Evaporator Steam	Rototherm Steam
$Ca(NO_3)_2$	1	28(82)	101(214)	125(257)	169(336)	133(272)
Standard	2	28(82)	102(215)	155(311)	171(339)	162(323)
Test	3	28(82)	102(216)	157(314)	179(338)	167(332)
HNO_3-HF	4	29(83)	102(216)	118(245)	154(310)	113(235)
Titanium	5	28(83)	102(256)	124(256)	159(318)	114(237)
Descaling	6	28(83)	102(216)	127(260)	155(311)	114(237)
	7	29(84)	102(216)	118(244)	149(300)	111(232)
AMCHEM 7-17	8	28(82)	102(216)	157(314)	169(336)	169(336)
Aluminum	9	28(82)	102(216)	160(320)	168(335)	164(327)
Deoxidizer	10	27(81)	103(217)	149(300)	158(317)	149(301)
	11	27(81)	102(216)	132(270)	151(304)	132(270)
	12	27(81)	102(216)	138(280)	150(302)	119(247)
	13	28(82)	102(216)	127(260)	150(302)	131(268)
AMCHEM 7-17	14	28(83)	103(217)	153(308)	161(322)	151(303)
Aluminum	15	28(83)	103(217)	143(290)	162(324)	154(310)
Deoxidizer & Alodine 600	16	28(83)	103(217)	132(269)	159(318)	149(300)
Ion-Exchange	17	27(78)	102(216)	147(297)	170(338)	167(332)
Regeneration	18	26(78)	102(216)	152(303)	163(325)	149(300)
Waste	19	26(78)	102(216)	146(296)	156(313)	133(272)

Aluminum Conversion Coating Solution

These tests, which were run at a steam temperature of 149-154°C (300-310°F) and a feed rate of 13.2 kg/hr (29 lb/hr), showed that a steam pressure of 485 kPa (70 psi absolute) was borderline for this operation. The evaporation level dropped below the acceptable level (70% at 14% solids feed) to 67% with insignificant variations in steam temperature and feed rate (Table 12, Tests 14-16).

Ion-Exchange Regeneration Waste

Since the ion-exchange regeneration waste contains only 3% solids, it must be evaporated 94% to obtain a 50% solids sludge. A feed rate of 12.2 kg/hr (27 lb/hr) and a steam temperature of 167°C (323°F) gave the required evaporation level (Table 12, Test 17). Lower steam temperatures (132-149°C/270-300°F), however, did not provide sufficient evaporation (83-87%) even at lower feed rates (10.0-11.8 kg/hr or 22-26 lb/hr, Table 12, Tests 18-19).

Summary of Evaporator Pilot Evaluation

The pilot test results provided sufficient information for production scale-up of the evaporator system. A Rototherm steam pressure of 690 kPa (100 psi absolute) was found to be optimum for concentrating a 3 to 15% solids influent to 50% solids. A pre-evaporator steam pressure of 345 to 690 kPa (50 to 100 psi absolute) was also found to be adequate for this operation. Using these steam pressures, ambient-temperature feed at rates up to 14.5 kg/hr (32 lb/hr) can be processed to 50% solids. The steam economy for evaporation of ambient temperature feed is 80%. Under these steam conditions, feed rates up to 34.0 kg/hr (75 lb/hr) can be handled if the influent is preheated to 100°C (212°F). In this case, a steam economy of 90% can be expected in the pre-evaporator and Rototherm units.

Crystallization in the evaporator, which may cause fouling of the evaporator heat-transfer surfaces, can be caused by using feed rates that are too low for the evaporator conditions. Fouling of the heat-transfer surfaces did not occur during pilot evaluation of the Rototherm evaporator system.

Evaporator Scale-Up and Economics

Scale-up of the evaporator system can be based on the evaporator economy, feed rate and heat-transfer area. To handle a waste stream of 5,680 l/day (1,500 gal/day) containing 25,000 ppm of nitrates (N), a 1.9-m^2 (20-ft^2), thin-film mechanically aided evaporator with a 2.4-m^2 (26-ft^2) pre-evaporator costing about $50,000 would be required. Steam at a pressure of 690 kPa (100 psi absolute) and at a rate of 1.25 kg steam/kg distillate (1.25 lb steam/lb distillate) would be used.

Analysis of the material costs required for treatment versus the sale price of the calcium nitrate fertilizer produced indicates that a net gain in material costs can be realized through lime treatment of nitrate-containing solutions. This is shown by the following example:

- Disposal Volume - 100,000 l (26,420 gal) per year of process solutions containing 35,000 ppm (N) and 10,000 ppm (F)

- Lime Slurry Concentration - 0.24 kg CaO/l (2.0 lb CaO/gal)
- Lime Treatment Level - 0.75 l of lime slurry/l of process solution (0.75 gal/gal)
- Lime Cost - $0.0358/kg CaO ($32.50/ton CaO)
- Annual Lime Cost - $640/year.

The lime-treated process solution is centrifuged to remove calcium fluoride and excess lime. After centrifugation, the solution contains 20,000 ppm (N) and 11.6% solids. The centrate is then evaporated to 50% solids at the following cost:

- Evaporator Economy - 80%
- Evaporation Level - 75%
- Steam Cost - $6.60/1,000 kg of steam ($3.00/1,000 lb of steam)
- Annual Steam Cost - $1,080/year.

The evaporator distillate contains less than 5 ppm (N) and is recycled or discharged. The evaporator bottoms are sold as calcium nitrate fertilizer for $0.33/kg of solids ($300/ton of solids) to give the following net gain:

- Annual Fertilizer Sales - $6,740/year
- Net Gain - $5,020/year.

The net gain does not include the savings realized by eliminating the cost of vendor disposal of waste solutions. Lime treatment of waste solutions having nitrate concentrations as low as 6,000 ppm (N) provides a breakeven point for material costs (Figure 23).

USE OF EVAPORATOR SLUDGE AS NITROGEN FERTILIZER

The feasibility of using evaporator sludge as nitrogen fertilizer was studied. This type of fertilizer would not be used at the start of the growing season because it does not supply potassium and phosphorous as a complete fertilizer does. It could be used as a sidedress or topdress fertilizer, however, during later growth stages. The use of fertilizer is instrumental in increasing crop yields and reducing growing costs. Because high energy inputs are required for fertilizer manufacture and because a critical worldwide shortage of fertilizer currently exists, use of recovered calcium nitrate sludge as a plant fertilizer would help to alleviate both situations.

The Long Island Vegetable Research Farm of Cornell University, Riverhead, New York (Figure 24), evaluated calcium nitrate sludge obtained from treated nitric-hydrofluoric acid descaling and Amchem 7-17 aluminum deoxidizer solutions. The two sludge samples were compared with certified ACS calcium nitrate obtained from the Fisher Scientific Company, Fair Lawn, New Jersey. Four varieties of lettuce were grown in a hydroponic culture in a glasshouse (Figure 25). Each type of fertilizer was used in a solution at normal strength and at 1.5 times normal strength.

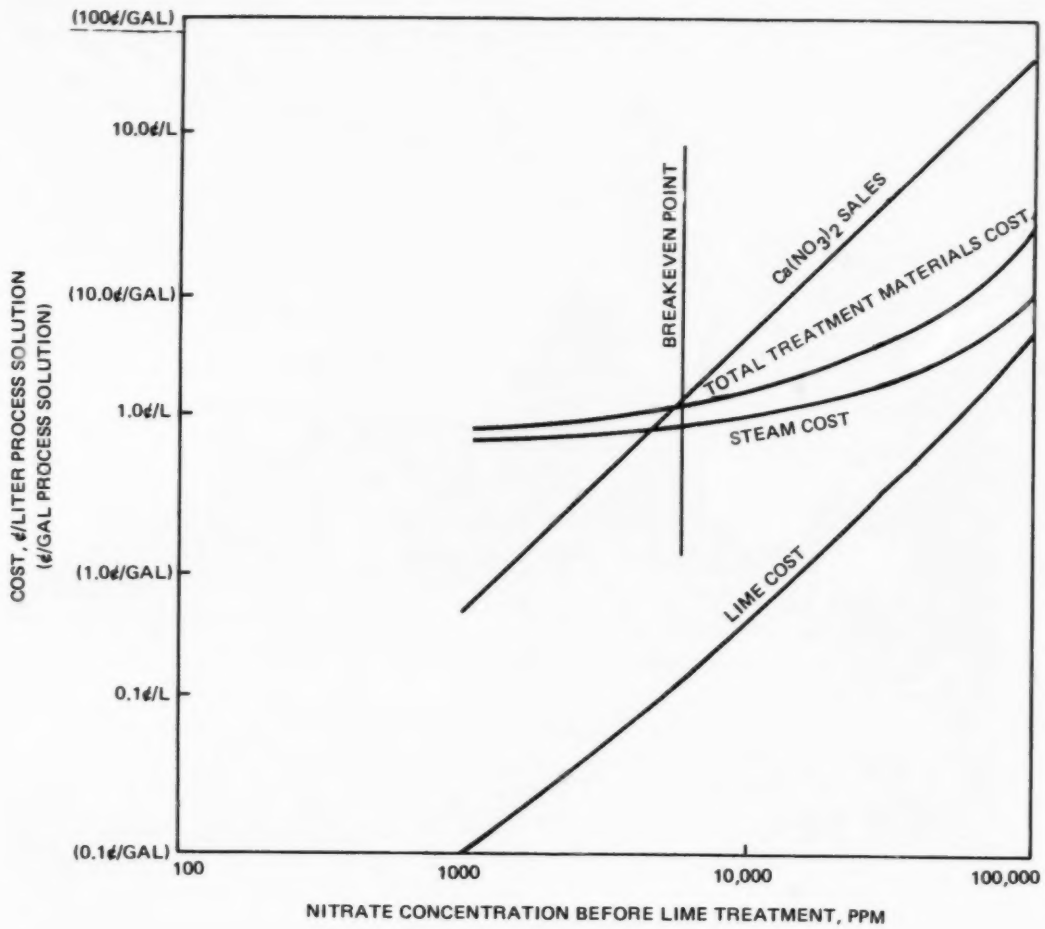

Figure 23. Material cost relationship for lime treatment and evaporation to remove nitrates vs. calcium nitrate sales.

Figure 24. Long Island Vegetable Research Farm of Cornell University.

Little variation was observed in the appearance of plants grown in the various fertilizer solutions (see Figures 26, 27 and 28). Differences in the plant type and growing medium (front to back in Figures 26-28) are apparent, though. The Long Island Vegetable Research Farm drew the following conclusion from their study: "No distinction could be made in growth of the plants, in yield of fresh material, in N-uptake by the plants, in dry matter content of the plants or N-content of the dry matter between plants grown in either of the experimental solutions or in the pure laboratory chemical."

Several other important attributes of the calcium nitrate sludge fertilizer were observed in this study. First, although phototoxicity is more evident in plants grown in a hydroponic system than those grown in soil, no trace of toxicity was present in plants grown with the sludge fertilizer. Second, because nitrogen fertilizer would be applied in later growth stages, soil leaching and contamination of groundwater would be minimized. Third, acidity of normally acid soils would be reduced upon repeated application of the sludge fertilizer - a beneficial effect for most crops. Details of the experiments conducted by the Long Island Vegetable Research Farm are contained in Appendix D.

CALCIUM FLUORIDE SLUDGE RE-USE

Re-use of calcium fluoride sludge as an additive to concrete was evaluated as a potential alternative to disposal of the sludge in landfills. This is becoming increasingly more important as landfill sites are being filled and disposal regulations are becoming more stringent. Sludge re-use in concrete would also eliminate the costs associated with landfill disposal.

The viability of the re-use concept, however, was dependent on whether the calcium fluoride sludge would maintain or increase the strength of the concrete. This was determined in the previous program. Flexural and compressive strength specimens were prepared from a standard concrete mixture and mixtures containing various percentages of calcium fluoride sludge as replacements for part of the concrete and part of the sand (Table 17). The specimens were tested in accordance with standard ASTM procedures. Test results (Table 17) indicate that flexural and compressive strengths are maintained if the calcium fluoride sludge is used only as a partial replacement for the sand while the percentage of cement in the concrete mixture is kept at the standard level (26.7%).

Leachability tests were also conducted to determine the extent of fluoride loss that would result from continuous exposure of the modified concrete to running water. Two liters (0.53 gal) of tap water were recirculated over a 45-g (0.1-lb) sample of Sludge Concrete Mixture No. 2 (see Table 17) for two weeks. An insignificant increase in fluoride content (0.068 to 1.7 ppm) occurred.

Additional testing will be required before calcium fluoride sludge recovered from lime-treated chemical process solutions can be used commercially. The strength and leachability tests did show, however, that addition of calcium fluoride sludge to concrete mixtures is a feasible waste disposal method that will reduce pollution disposal costs and dependency on landfill sites.

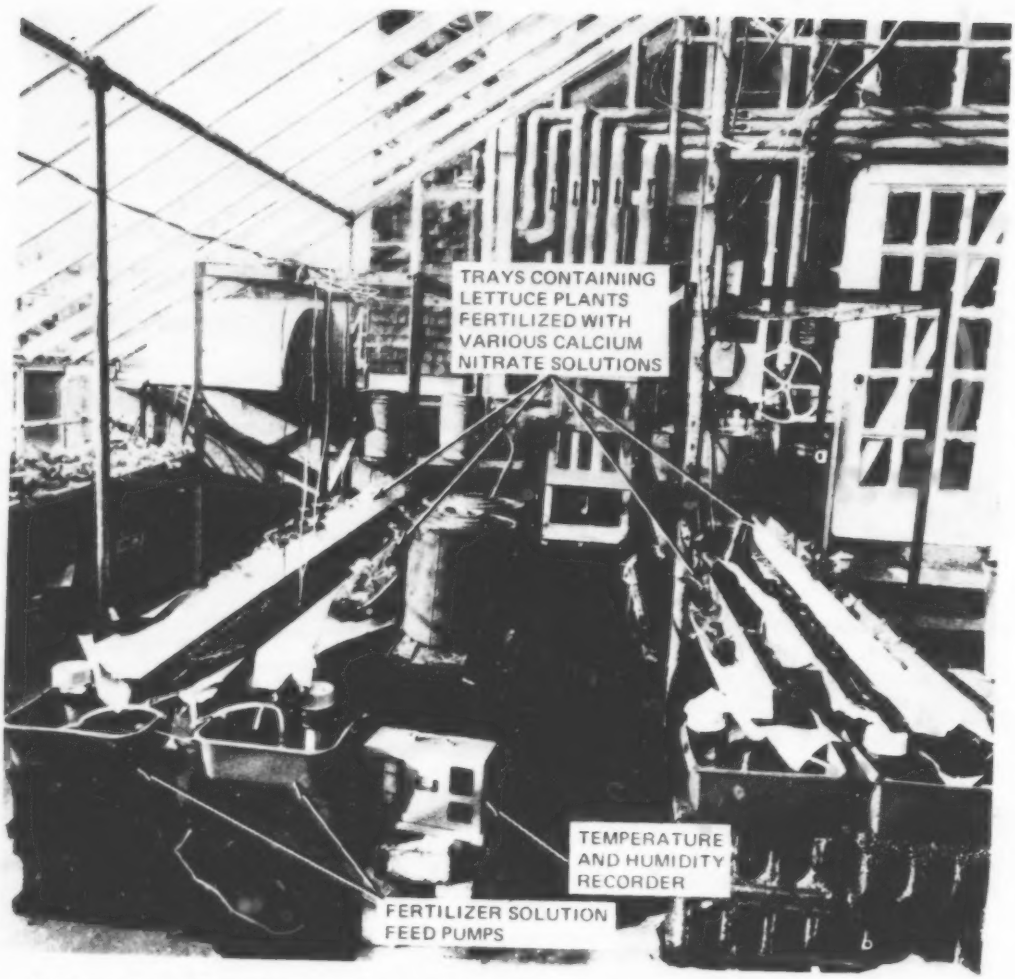

Figure 25. Glasshouse containing calcium nitrate fertilizer test setup.

Figure 26. Lettuce grown with calcium nitrate fertilizer obtained from treated aluminum deoxidizer solution.

Figure 27. Lettuce grown with normal-strength calcium nitrate fertilizer obtained from treated nitric-hydrofluoric acid descaling solution and standard calcium nitrate.

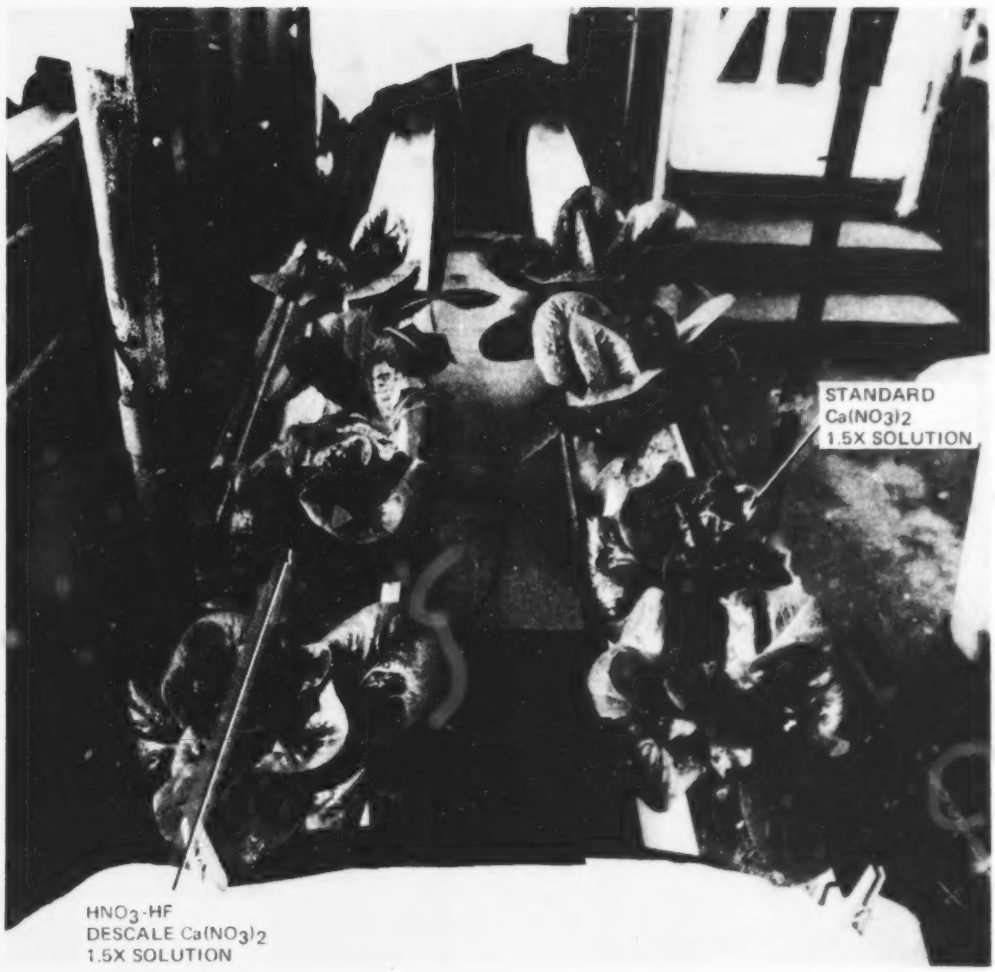

Figure 28. Lettuce grown with 1.5 times normal strength calcium nitrate fertilizer obtained from treated nitric-hydrofluoric acid descaling solution and standard calcium nitrate.

TABLE 17. FLEXURAL AND COMPRESSIVE STRENGTH TEST RESULTS FOR REGULAR AND SLUDGE-CONTAINING CONCRETES

Mixture No.	Ratio of Cement To Solids	Percentage of Cement	Percentage of Sand	Percentage of Sludge	Average Flexural Strength kPa (psi) 3 Tests	Average Compressive Strength kPa (psi) 6 Tests
1	1:2.75	26.7	73.3	0	3820 (554)	16100 (2330)
2	1:3.16	24.1	66.4	9.5	2640 (383)	11800 (1705)
3	1:2.75	26.7	66.5	6.8	3790 (550)	20000 (2895)

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APPENDIX A

PROCEDURE FOR ANALYSIS OF FLUORIDE

The total fluoride concentration in various samples was determined with an Orion F^- Specific Ion Electrode using the Orion-recommended, known addition procedure. Preliminary sample preparation varied depending on the concentration of fluoride and other ions in the samples.

The following procedure was used:

1. Distill the sample to prevent precipitation after addition of sodium citrate buffer.

2. Prepare a buffered sample solution based on the approximate fluoride concentration in the sample.

   a. For fluoride concentrations less than 10 ppm, add 10 ml of saturated sodium citrate to a 90-ml sample and adjust the pH to 8.

   b. For high fluoride concentrations, mix an aliquot of the sample with saturated sodium citrate to give a fluoride concentration of about 100 ppm. Adjust the pH to 9.5-10.

3. Measure the electrode potential of 100 ml of buffered sample using an Orion F^- Specific Ion Electrode.

4. Add 10 ml of a standard solution (about ten times the anticipated concentration of the sample) and then measure the electrode potential.

5. Determine "ΔE," the difference between the initial potential (buffered sample) and the final potential (with standard solution added).

6. Using the known addition table on Page 8 of the Orion Research Analytical Methods Guide, determine "Q" corresponding to "ΔE."

7. Calculate the concentration of the original sample by multiplying "Q" times the concentration of the standardizing solution.

APPENDIX B

PROCEDURE FOR ANALYSIS OF NITRATE IN CALCIUM NITRATE

The nitrate content in calcium nitrate was determined by an oxidimetric procedure (1) which involved reduction of nitrate to nitrite by excess ferrous ion and measurement of the remaining ferrous ion by back titration with potassium dichromate.

The following procedure was used:

1. Weigh out an amount of sample such that 25 ml of the solution contains 25-80 mg of nitrate.

2. Dissolve the sample in water and filter if the solution is turbid.

3. Transfer 25.00 ml of the solution to an Erlenmeyer flask.

4. Add 25.00 ml of 0.2N ferrous sulfate solution and 20 ml of concentrated (6-8 molar) sulfuric acid.

5. Boil the solution for 3 minutes to complete reaction.

6. Prepare a blank containing 25.00 ml of 0.2N ferrous sulfate solution and 20 ml of concentrated (6-8 molar) sulfuric acid to run at the same time.

7. Titrate the cooled solution with 0.1N potassium dichromate using ferroin as an indicator. Average error has been determined to be ±0.2 percent.

(1) Leithe, W. 1948. Oxidimetric Nitrate Analysis of Fertilizers and Other Commercial Products. Anal. Chem., Vol. 20, pp. 1082-1084.

APPENDIX C

PROCEDURE FOR ANALYSIS OF NITRATE IN WATER SAMPLES

The nitrate content in water samples was determined by the EPA automated cadmium reduction method using a Technicon Autoanalyzer. The nitrates are reduced to nitrites with a cadmium-copper catalyst and then reacted with sulfanilamide to form the diazo compound. This is coupled in an acid solution (2.0 - 2.5 pH) with N-1-naphthylethylenediamine hydrochloride. The azo dye intensity, which is proportional to the nitrate concentration, is then measured with a colorimeter having a 540-μm filter.

The following procedure was used:

1. Set up the manifold (Figure 29). Note that the reductant column should be in a 20-degree incline position with copper at the lower end.

2. Allow both the colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust the dark current and operative opening on the colorimeter to obtain a stable baseline.

3. Place appropriate nitrate standards in order of decreasing nitrogen concentration. Complete loading of sample tray with unknown samples.

4. Switch sample line to sampler and start analysis.

5. Compute concentration of samples by comparing peak heights with standard curve.

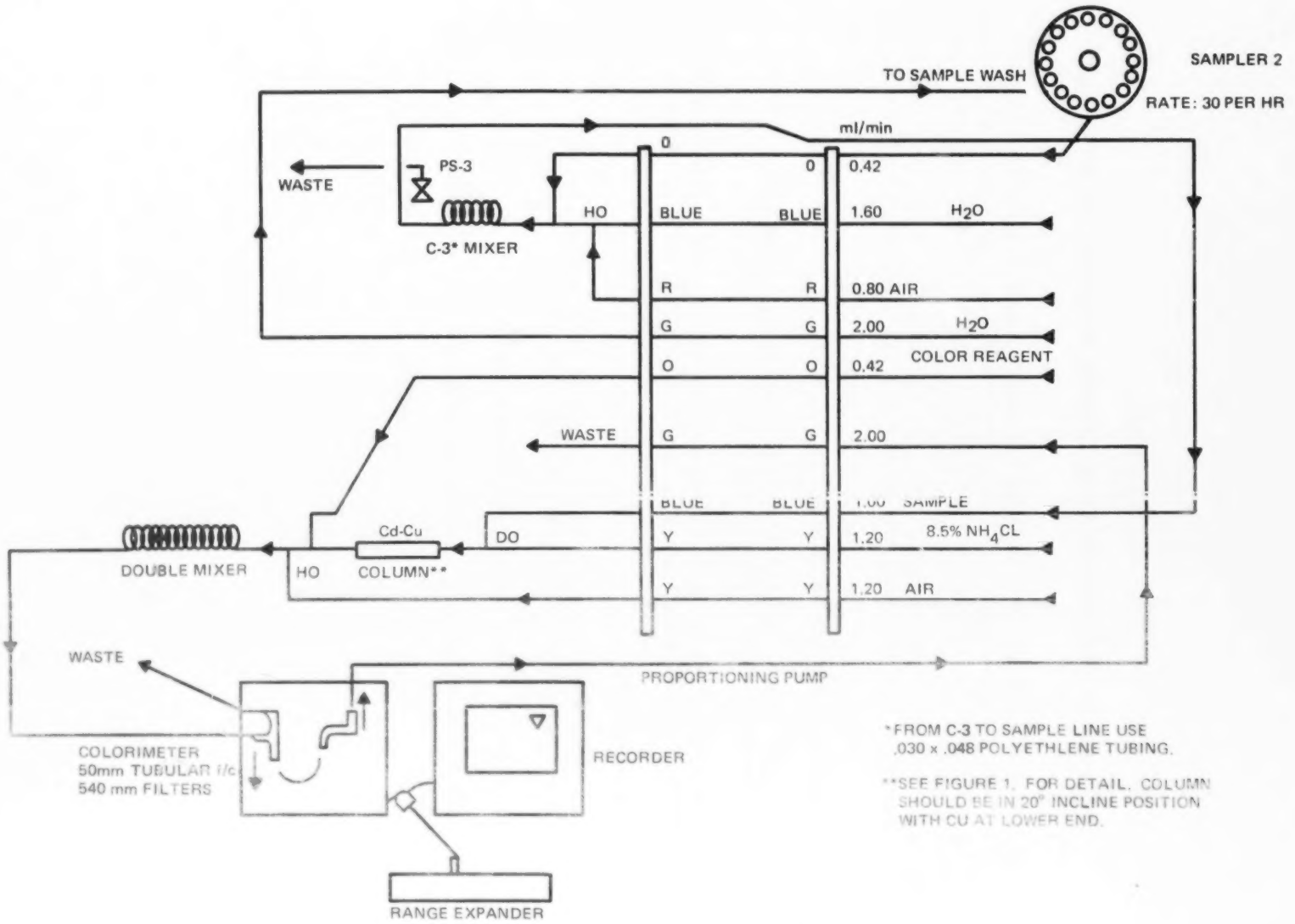

Figure 29. Nitrate-nitrite manifold.

APPENDIX D

TEST OF TWO WASTE PRODUCTS OF GRUMMAN AEROSPACE CORPORATION AS A SOURCE OF NITROGEN FERTILIZER

P. A. Schippers

Long Island Vegetable Research Farm

(Cornell University)

Riverhead, N. Y. 11901

Products:

1. Nitric-HF, descale fertilizer, 17.4% nitrogen (in this report called Descale).

2. 7-17 deox fertilizer, 13.6% nitrogen (further called Deox).

Comparison:

The test products were compared with Certified A. C. S. calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) obtained from Fisher Scientific Company, Fair Lawn, New Jersey 07410 (Catalog C 109, Lot 743725) with the following impurities:

	ppm
Insoluble matter and NH_4OH	40
Barium (Ba)	30
Chloride (Cl)	20
Heavy metals (as Pb)	1
Iron (Fe)	1
Magnesium and Alkalies (as SO_4)	1500
Sulfate (SO_4)	20

Crop: Lettuce.

Varieties: 1. Iceberg (Hart's Seeds), crisp, heading type.

2. Parris Island (Harris Seeds), Cos or Romaine type.

3. Buttercrunch (Harris Seeds), Bibb type.

4. Salad Bowl (Harris Seeds), looseleaf, non-heading type.

Growing system:

Hydroponics: for part of the growing season without any rooting medium, for later part of the season with Perlite* (super-coarse grade) as medium; in glasshouse.

Description of the Experiment:

Sowing: On October 27, 1975, seeds were sown in either Kys-kube** growing blocks or in a bed of horticultural Perlite of propagating grade. The blocks and the bed were flushed once a day for one hour with nutrient solution of 0.25 of the normal strength from October 27 until November 3, 1975, 0.50 of the normal strength from November 4 until November 7, and 0.75 of the normal strength from November 8 until November 24, 1975. After transplanting on November 24, the full strength was given.

Growing: On November 24, plants growing in the Perlite bed were transplanted into 5.7cm (2.25 in) peat pots filled with Perlite of propagating grade. The pots were slashed with a knife at the bottom corners to facilitate the uptake of nutrient solution and to give the roots a better opportunity to grow out of the pot into the nutrient solution.

The plants in Kys-kubes and peat pots were placed in 3-m-long plastic roof gutters through which nutrient solution flowed continuously. Two plants of each variety in the Kys-kubes and two plants in peat pots were placed in each of four gutters and the gutters were supplied with nutrient solutions either at normal strength or at 1.5 times the normal strength.

The nitrogen was supplied either in the form of Descale or in the form of the pure calcium nitrate from Fisher.

On December 11, two more gutters which had been used for a different experiment were prepared for the Deox fertilizer. Plants for these gutters were taken from the corresponding Descale gutters. After that date, the setup was as follows:

---

*Perlite is heated and expanded volcanic rock. It has no buffering capacity and does not contain any nutrients for the plant. Plant roots may extract some sodium and aluminum.

**Kys-kubes are growing blocks, 5.1 cm (2 in) high and 5.1 cm X 5.1 cm (2 in X 2 in) at the base, consisting of a blend of organic and inorganic materials with starter fertilizer.

Gutter	Concentration of nutrients in solution	Form of calcium nitrate
1	1	Deox
2	1.5x	Deox
3	1x	Laboratory chemical
4	1x	Descale
5	1.5x	Descale
6	1.5x	Laboratory chemical

The eight plants in each gutter were placed at 30-cm distances: one plant of each variety in Kys-kubes, the other in peat pots with Perlite.

Nutrient solutions: The macro nutrients were supplied by KH_2PO_4, $MgSO_4 \cdot 7H_2O$, K_2SO_4, all as pure laboratory chemicals, and calcium nitrate either in the form of the laboratory chemical $Ca(NO_3)_2 \cdot 4H_2O$ or in the form of Descale or Deox. KOH was used to adjust the pH to approximately 6.5.

The following micro-nutrients were given, also as pure laboratory chemicals (except for the iron):

Fe: 10 ppm as Sequestrene

B: 0.47 ppm as H_3BO_3

Cu: 0.02 ppm as $CuSO_4 \cdot 5H_2O$

Mn: 0.65 ppm as $MnSO_4 \cdot H_2O$

Mo: 0.05 ppm as $Na_2MoO_4 \cdot 2H_2O$

Zn: 0.12 ppm as $ZnSO_4 \cdot H_2O$.

The composition of the nutrient solutions in parts per million was:

	Gutter 1, 3, 4 (Normal)	Gutter 2, 5, 6 (1.5 x Normal)
K^+	280	420
Ca^{++}	180	270
Mg^{++}	50	75

	Gutter 1, 3, 4 (Normal)	Gutter 2, 5, 6 (1.5 x Normal)
$NO_3^-(N)$	120	180
$H_2PO_4^-$	30	45
SO_4^{2-}	160	240

The total volume of nutrient solution in each gutter (including catch basin and supply tank) was 10 l before and 25 l after adding Perlite to the gutters. The Perlite was added after the first harvest on January 12, 1976, in order to prevent the plants from falling over, since they became too top-heavy for the size of the Kys-kubes and peat pots and the roots had nothing to hold onto.

The old solutions were replaced by fresh ones every three weeks.

Temperature: Night temperature was maintained at 15°C (59°F) until December 12, 1975, and then increased to 20°C (68°F). Day temperature was maintained at 20°C (68°F) until the same date, then increased to 25°C (77°F), but on sunny days, day temperatures could go as high as 30°C (86°F).

Notes on the growth of the plants: Since the intensity of natural daylight is at a minimum during the time of the year in which the experiment was started, not too much was expected of the growth of the crop. However, although growth was slow at first, it picked up considerably during the later part of the growing period.

Some varieties were clearly more suitable for this type of growing than others. The Iceberg lettuce did not head well, grew slowly and confirmed its reputation of not being suitable for greenhouse growing. The Salad Bowl variety grew well, but for some unknown reason started to bolt quite soon, a phenomenon which did not occur in other experiments. For these reasons, and also to obtain some interim data, these two varieties were harvested much earlier than the others which grew well.

The plants grown in the Kys-kubes grew far better than those grown in peat pots with Perlite.

There was neither any visible differences in the growth of the plants grown with the experimental fertilizers and those grown in the pure chemical, nor between the plants which had received nutrient solutions of normal strength and those which had received the stronger solutions.

Harvest:

On January 12, 1976, the heads of Iceberg and Salad Bowl were harvested and weighed. Each head was cut into small pieces and dried in an oven at 70°C (158°F) for 16 hours, weighed again, ground in a Wiley mill and stored for future chemical determinations. The same procedure was applied on February 3, 1976, with Parris

Island and Buttercrunch varieties, with the only difference that only half or quarter plants were dried. This was done because of their size. The heads were cut from bottom to top, making sure that all tissues were represented proportionally.

Results:

The results (Table D-1) were statistically analyzed by analysis of variance to show the responses of the plants and the significance of the results.

Although there were some significant interactions between some of the variables, the source of nitrogen was not involved in any of these interactions with the exception of the interaction between source of nitrogen and variety and between source of nitrogen and concentration. Therefore, a discussion of these interactions will be omitted except for the two mentioned above.

Yield: For the purpose of this report the only interest would be in whether or not the source of nitrogen had a significant effect on yield. According to the analysis of variance it had not, meaning that results with both Descale and Deox were indisguishable from those obtained with the pure chemical.

Percentage dry matter: Also in this case the source of nitrogen had no statistically significant influence.

Percentage nitrogen in the dry matter: Again, the source of nitrogen had no influence, but the concentration of the fertilizer in the nutrient solution affected the nitrogen content of the dry matter. An increase in fertilizer concentration resulted in a higher nitrogen content, a result which was expected.

The two interactions mentioned before were at the 5% probability level. The one between source of nitrogen and variety meant that not all varieties reacted in exactly the same way to the source of nitrogen. The variety Salad Bowl, for instance, had the highest nitrogen concentration (4.57%) with the pure chemical and the lowest (3.88%) with the Deox, whereas the variety Buttercrunch reacted in reverse (4.04 and 4.25%).

The interaction between source of nitrogen and concentration of the nutrient solution meant that the differences in nitrogen content caused by the concentration were smaller if the plants had grown in Descale or Deox than if they had been grown in the pure chemical. These differences in reaction, however, were of little practical value.

Nitrogen uptake per plant: The source of nitrogen was of no significance.

Conclusion:

No distinction could be made in growth of the plants, in yields of fresh material, in N-uptake by the plants, in dry matter content of the plants or N-content of the dry matter between plants grown in either of the experimental solutions or in the pure laboratory chemical.

TABLE D-1. AVERAGE RESPONSE OF LETTUCE TO VARIOUS TREATMENTS

Source of Variation	Yield of Fresh Material, g/plant	Dry Matter, %	Nitrogen in Dry Matter, %	Nitrogen Uptake per Plant mg
Variety				
Iceberg	37 a	5.54 a	3.97 a	83 a
Parris Island	345 b	5.42 a	4.01 a	747 b
Buttercrunch	258 c	4.93 b	4.15 a	531 c
Salad Bowl	108 d	5.24 a	4.35 b	243 d
Nitrogen source				
Pure chemical	195	5.13	4.15	401
Descale	172 ns	5.29 ns	4.11 ns	360 ns
Deox	195	5.42	4.10	443
Concentration				
1 x normal	186	5.20	3.96 a	384
1.5 x normal	188 ns	5.36 ns	4.27 b	419 ns
Substrate				
Kys-kubes	223 a	5.24	4.26 a	485 a
Peat pots	152 b	5.32 ns	3.98 b	320 b

ns: Differences are not statistically significant.

a,b,c,d: Differences between treatments followed by different letters within each group are statistically significant; differences between those followed by the same letters are not.